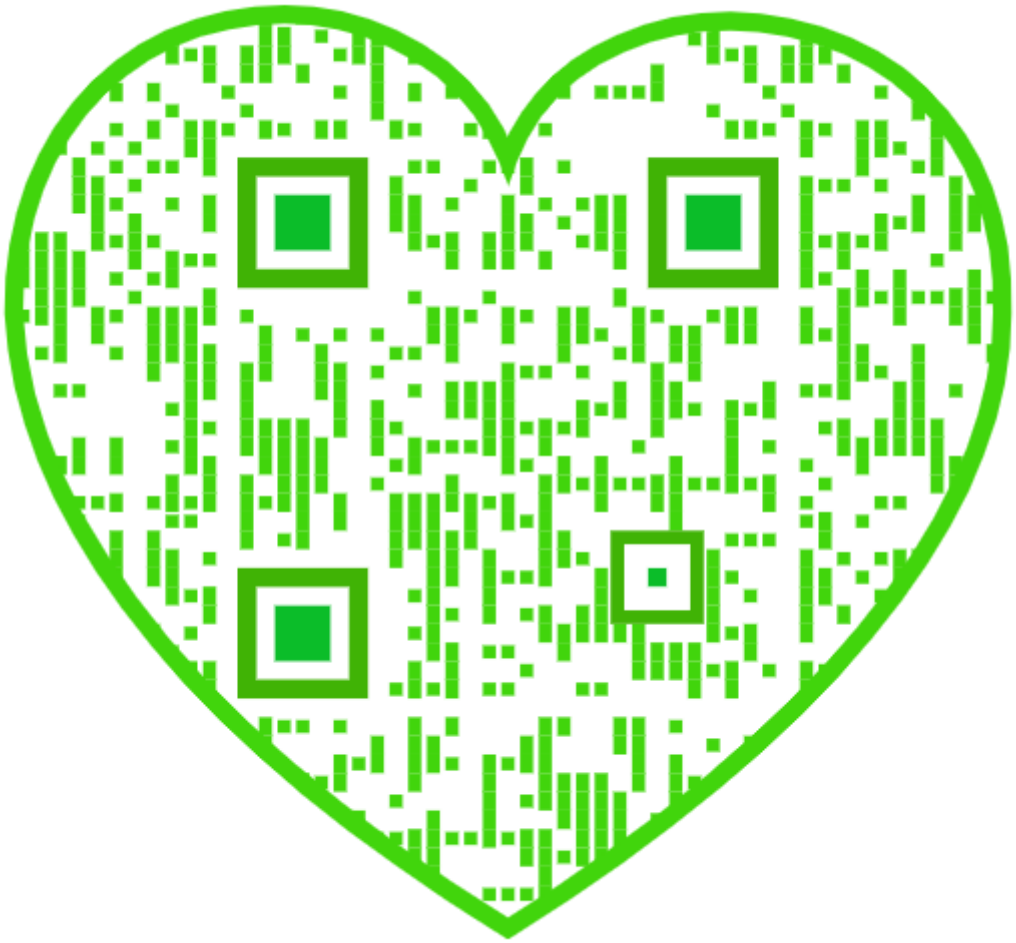

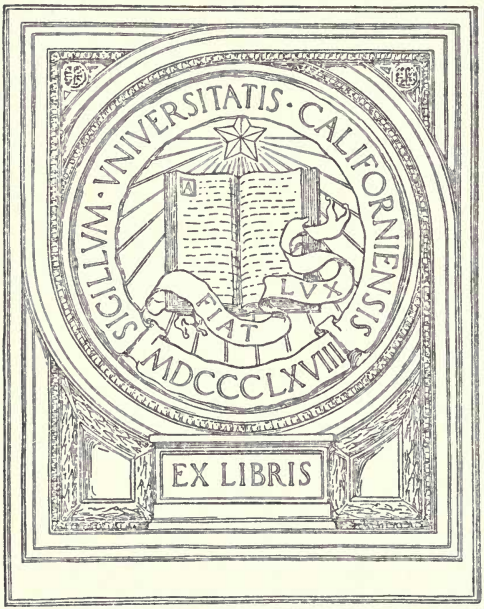
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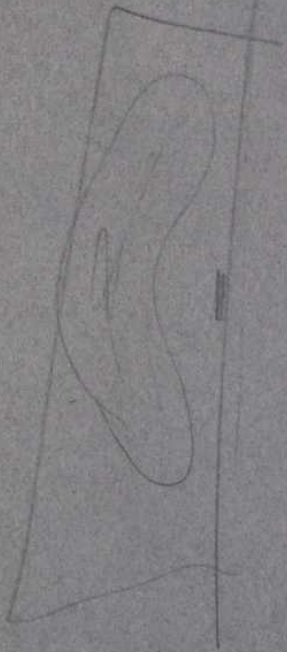

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...THE...

CHEMISTRY OF POTTERY

—— BY ——

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CHEMIST OF THE AMERICAN ENCAUSTIC

TILING COMPANY, ETC.

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1895.

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DEDICATED

TO MY

ASSOCIATE IN CERAMIC WORK,

HERMAN C. MUELLER,

SCULPTOR.

CONTENTS.

			Page.
Chapter	I.	Analysis of Pottery Materials and Products	1
"	II.	Physical and Empirical Tests	15
"	III.	Pyrometry	26
"	IV.	Classification of Ceramics	41
"	V.	Pottery Glazes	48
"	VI.	Red Ware	58
"	VII.	Rockingham and Yellow Ware	66
"	VIII.	Stoneware	77
"	IX.	Raw Materials of White-Ware Bodies	93
"	X.	White Granite and Cream-Colored Ware	117
"	XI.	Majolica and Enameled Tile	127
"	XII.	White Enameled Brick	139
"	XIII.	Floor-Tile and Terra-Cotta	149
"	XIV.	Refractory Materials	158
"	XV.	Burning the Ware	175

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LIST OF ILLUSTRATIONS.

Plate 1. From the author's collection ..... Frontispiece.
" 2. Clay Bank, Muskingum Co., Ohio ..... to face p. 97.

Page.
Initial 1
" 15
Vicat's Needle 19
Gas Trial Kiln 23
Initial 26
A Seger Cone in Natural Size 36
Initial 41
Tailpiece 47
Initial 48
Tailpiece 57
Initial 58
" 66
" 77
" 93
" 117
" 127
Tailpiece 138
Initial 139
" 149
" 158
" 175
Kiln Barometer or Draught Meter 178

PREFACE.

The pottery industries of England and America have afforded chemists little opportunity for systematic work, so that they have remained largely on an empirical basis and have supplied nothing of moment to chemical technology.

With the exception of the excellent treatises on porcelain, but little work relating strictly to pottery has been published in France.

The best of such work, accessible to chemists, is that of German ceramists and has appeared in that excellent technical periodical, "Die Thonindustrie-Zeitung," founded by the late Professor Seger, sometime chemist of the Royal Porcelain Factory at Charlottenburg, near Berlin.

Most of the technical publications on pottery, in book form, dwell on the mechanical technology of the clay industries, the chemical parts consisting merely of receipts, claiming a practical origin.

Such receipts are almost altogether without value, as the materials specified are not characterized by accompanying analyses and the temperatures to which the products are to be subjected are not given, or not determined in a way that they can be fixed with certainty.

While to many of our chemists, engaged in developing the natural resources of the country the clays found on every side have seemed to offer a fruitful field for investigation, the information at command concerning the chemical needs of the potter has been so meager, that their efforts have been practically abortive. The thousands of analyses published are mostly worthless, because they do not go far enough or because unaccompanied by essential physical tests and practical trials.

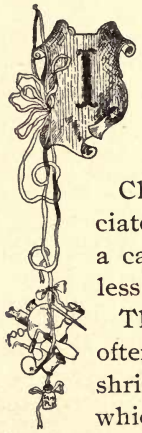
It is hoped that this little treatise will supply information that will turn future labors in this channel to good account.

The writer is well aware that in confining the subject matter to the results of his personal experience the shortcomings of the treatise are numerous and manifest; but he believes that as such it is a more direct expression of the practical needs of the working potter, and therefore of more immediate value, than a compilation of the published work of European chemists on their ceramic industries.

In a treatise of this kind, only the essentials, pottery bodies and glazes, could be considered. The colors and operations of decorating, though interesting objects of chemical study, would have led too far from the main purpose of the book.

CHAPTER I.

ANALYSIS OF POTTERY MATERIALS AND PRODUCTS.



IT IS most difficult to convey to the public the necessity of exercising the greatest care in taking the sample of a clay for examination.

Chemists and engineers will, of course, appreciate this, though they often do not realize that a carelessly taken sample is absolutely worthless for even a preliminary test.

The usefulness of a clay for a given purpose often hinges on a slight point of plasticity and shrinkage or color at a certain temperature, which may either have been imparted to it, or taken away from it, by a few years weathering at the exposed outcrop of a deposit, or by the infiltration, or washing out, at that point, of small amounts of iron, lime, or alkalis.

The first rule in clay examinations, then, is that a clay deposit which does not warrant the expense of thorough sampling does not justify even a preliminary examination,—for we have not, as in iron-ore, for example, a constituent which must be contained in at least a certain amount, and which any exposure is not likely to

materially vary, nor are there constituents which must be practically absent.

Every constituent of a clay is valuable. It is the work of the chemist to determine to what use it can be put; and, considering its constituents, to what conditions of manufacture it must be subjected.

His first question, then, is, whether there be enough like the sample to warrant difficult tests.

If the clay be not too hard, and superimposed strata too difficult to work, it is best to take the samples over a larger area by systematic borings, using a one and one-half to two-inch pod-auger, welded to a section of gas-pipe for the purpose.

If the overlying strata are sandy or otherwise liable, by dropping down into the bore-hole, to vitiate the character of the sample, it becomes necessary to exclude them by driving down a section of tubing of suitable width to the top of the clay stratum which is to be sampled.

If sampling by boring be not practicable, the deposit must be opened at as many exposures as is practicable and laid bare, if possible, through its entire depth, well beyond the frost line or other surface influence, and the sample there taken down the whole exposed face of the vein.

The sampling down of the clay obtained by these various means is done in the manner familiar to all accustomed to handling ores, and should be done in the laboratory, if the man in the field is not perfectly familiar with the process.

In preparing a sample of clay for chemical analysis, it is important to bear in mind what constituents, separable by mechanical means, the clay contains which are objectionable in the industry in which it is likely to be used, and to reject, by a suitable treatment, from the analytical sample, those constituents that will not enter into the ultimate product, though it is, of course, necessary to at least approximately determine their character and amount, as this determines the future mechanical purification process to which such a clay, if used, would have to be subjected.

Thus "lime-dogs" and pebbles are objectionable in terra-cotta, brick and red ware clays, and are customarily removed, if present, by screening the dried and crushed clay through a sieve of ten to twenty meshes to the inch.

Coarse sand and particles of iron-pyrites are objectionable in finer terra-cotta, floor tile and yellow ware, and are removed by disintegrating the clay in water, passing the "slip" through a sieve of sixty meshes to the inch, and drying the purified clay.

In clays for finer ware, flakes of mica, in addition to the last mentioned impurities, are objectionable, and must be removed by passing the "slip" through a 100 to 120 mesh sieve.

It may seem superfluous to say that the chemical analysis of a clay should be as accurate as possible; yet the very considerable number of slovenly analyses published yearly would seem to make it necessary to insist upon this point.

By far the greater number of technical analysts are engaged in making single determinations, and not complete analyses of the substances with which they have to deal. Clays, in which all the constituents are of equal importance, seem, therefore, to many as difficult as they certainly are tedious, to analyze, and the determinations of their various constituents are treated as if they were a collection of individual determinations, the incorrect footing up of which is an "arbitrary impertinence," which may be ignored.

While it is true that the chemical analysis alone, however accurate, is insufficient without accompanying physical tests, to give one a perfect characterization of a clay, its value is sufficiently great to warrant the most careful work.

Although the scope of this book makes it necessary to refer to works on analytical chemistry for the details of clay analysis, it seems desirable to point to special considerations upon which text-books do not sufficiently insist.

The character of a clay depends largely upon the mutual proportions of alumina and silica, so that, although these are generally the largest constituents of a clay, it is important that they be determined with particular accuracy.

In spite of the various and detailed descriptions of the treatment of the residue of the acidified fusion of a clay with alkali carbonates, it seems practically impossible to accurately separate silica from the alumina group, and to obtain both without mutual contamination. The writer, therefore, thinks it indispensable to finally obtain the

proportion of silica by difference, smoking off that obtained from the fusion of the clay with alkali carbonates, with hydrofluoric acid, taking cognizance of the residue obtained from this operation.

The alumina and ferric oxid precipitate must similarly be obtained by difference, when the silica, which it almost invariably contains, has been separated by dissolving the weighed precipitate in Mitscherlich's mixture, or, if very refractory, by fusion in acid potassium sulfate, the silica, after weighing and volatilizing as fluorid, being, of course, added to the main portion.

Occasionally, the errors due to alumina in the silica and silica in the alumina group mutually compensate each other within the limits of ordinary analytical accuracy. It is, however, a dangerous practice to depend upon such a balancing of errors.

It must further be borne in mind that the common impurities of analytical reagents are the normal constituents of clays, and may frequently throw out an accurately manipulated analysis several per cent.

Hydrochloric acid and ammonia frequently contain very appreciable traces of alumina and soluble silica. Precipitated calcium carbonate (if Lawrence Smith's alkali determination be used) cannot be bought free from alkali, and dry sodium carbonate contains, almost invariably, traces of silica, and has not infrequently been found by the writer to contain fine splinters of parian, from the "porcelain" linings, possibly, of the mills in which it was ground, whereby silica and alumina would both be introduced into the analysis.

Distilled water is also a very fruitful source of difficulty; for in washing the bulky precipitates occurring in clay analyses, traces of impurity rapidly heap up to important factors. Trouble has been found with water which, it was supposed, had been distilled with great care and condensed in a block-tin worm that could not be suspected. Still the latter proved to be the source of the difficulty. The upper coil, into which the hot steam enters, had, in the course of two years, become highly crystalline, and was riddled with fine cracks. Into the latter, the cooling water had seeped and vitiated the distillate.

Such a defect in the condensing worm may readily be detected by drawing the cooling water from the tub, and now blowing the steam from the still into the coil. Presently the mud and scale deposited on the latter are dried through the heating of the worm. If now little spots of the same remain persistently damp, it becomes apparent that underneath are cracks in the worm sufficient to let the steam through, and sufficient, also, when the tub is filled, to give the cooling water access to the interior of the worm.

In the case of clays containing a larger amount of alkali, if potash and soda be not separated, but the titer of the chlorine found in the weighed chlorids, and the equivalent oxids calculated, it is important to give the combining weight of the alkali obtained, so that the chemical formula of the clay may be calculated, in case it should be desired to use it as or in a glaze.

Beside the ultimate analysis, a proximate one is very

important. Considering the formation of clays, it will be appreciated that its various ultimate constituents are grouped in a variety of mixed minerals of widely differing physical properties, and that these, rather than the former, determine the character of the clay.

An accurate separation of the clay into its various component minerals is, in the present state of analytical knowledge, out of the question; yet, the well-known separation of mineral and quartz sand, by digesting the clay in strong sulfuric acid, and after washing out the excess of acid and the sulfates formed by the decomposition of the clay substance proper and the micaceous minerals, and removal of the separated soluble silica with a solution of alkali carbonate, described in text-books on analytical chemistry, gives data of great practical value.

When the sand thus found in a clay is not pure quartz, but, as is generally the case, consists of the detrital matter of a great variety of minerals, it becomes very difficult to estimate its probable effect in its influence on the refractory qualities of a clay, and the resulting coefficient of expansion of the burned body. For minerals, more or less fusible, greatly reduce the refractoriness of a clay, while quartz, at moderate temperatures (though not at high ones), increases it; and with reference to the coefficient of expansion, the effect of these substances is also diametrically opposite.

As now, there is no way of determining in a mixture of quartz and mineral sand how much of the silica belongs to the minerals and how much to the quartz itself,

Seger and Aron[1] have suggested that, inasmuch as the mineral detritus of the sand is more or less fusible, and plays the same rôle in a pottery body as powdered feldspar, a substance with the action of which, in a clay, the potter is perfectly familiar; and as, further, such mineral sand is often mainly feldspathic, it is, for all practical purposes, sufficient to consider it feldspar.

Hence, the alumina obtained on analyzing the sand is used as the factor with which the silica to be assigned to the mineral sand is determined, its weight being multiplied by the factor expressing the proportion of silica to alumina in feldspar, and this amount of silica being deducted from the total silica of the sand, the remaining silica is called quartz, while that deducted, together with the alumina and the alkalis and alkaline earths found in the sand, are added, and designated "feldspathic" sand or detritus.

The difference between the weights of the constituents found in the complete analysis of the clay and those of the sand, left by the sulfuric acid and alkali carbonate treatment, are calculated as constituting the "clay substance." In order that the proportion of the latter may be more satisfactorily surveyed and compared with those of kaolinite, it is necessary to reduce them to a basis of 100.

The "rational analysis," then, looks upon every clay as consisting of a "clay substance" deviating more or less from kaolinite, in which the alumina is substituted,

[1] Notizblatt des Töpfer-u. Ziegler-vereins, *1874*, S. 226, and Zwick, Jahresbericht, *1878*, S. 21, and *1879*, S. 41.

to a greater or less degree, by ferric oxid, etc., and the combined water by alkalis and alkaline earths; quartz, in a finely divided state, and mineral sand, practically feldspathic.

Scientifically, it must be conceded Dr. C. Bischof that the result is "ein künstlich theoretisches Bild,"[1] both on account of the assumption underlying the calculation of the mineral sand as feldspar, and because the method of separating the mineral and quartz sand from the clay substance is by no means an accurate analytical process.

Thus a pure feldspar (orthoclase) treated in the same manner as the clays are treated,[2] left in one instance a residue of 81.44 per cent., and in another 83.95 per cent.

In the hope that clays might be decomposed with diluted sulfuric acid under pressure under conditions that would cause less action on feldspathic minerals, it was found that two grams of kaolin treated with twenty cubic centimeters of five times normal sulfuric acid in a sealed tube of hard glass, was only completely decomposed in two hours, at a temperature of 200° C., conditions that were insufficient for decomposing some plastic clays. Yet a feldspar subjected to the same treatment, left after separation of the acid and washing out the soluble silica with solution of sodium carbonate, a residue of only 82.67 per cent., practically the same as the regular treatment.

It is hardly possible then, with existing methods, to

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[1] Böckmann: Untersuchungs methoden, S. 354, *1884*.

[2] Fresenius: Anleitung zur Quantitativen Chemischen Analyse, Sechste Auflage, ii, 352, f.

dissolve the "clay substance" out of a clay without a loss of feldspar that may reach twenty per cent. of the amount present.

The treatment with sulfuric acid even affects the quartz to some extent and leads to its removal by the subsequent sodium carbonate treatment.

Thus a pure finely powdered quartz was found to contain 3.75 per cent. silica soluble in sodium carbonate solution. Subjected after removal of the same to the treatment used for solution of "clay substance," it lost 3.88 per cent. apparently rendered soluble by the action of the sulfuric acid.

Practically, this division of the analytical data of clays is of the greatest service to the potter, who is familiar with "clay, flint, and spar," and knows how to vary their proportions for his various ends. It has resolved the composition of natural clays into components with which he knows how to deal, and made once unintelligible analyses serviceable to him.

The following may serve as an example of the analysis of a clay, conducted on these lines. It is a kaolin from Nelson County, Virginia.

	The entire clay.	The contained sand.
Silica	50.02	12.62
Alumina	35.18	1.72
Ferric oxid	0.36	0.09
Lime	0.12	0.06
Magnesia	0.07	0.02
Alkalis	3.39[1]	1.08[2]
Combined water	10.57	0.00
	99.71	15.59

[1] Combining weight 43. [2] Combining weight 34.2.

	Rational Analysis.
Clay substance	84.12
Feldspathic detritus	9.04
Quartz	6.55
	99.71

	PERCENTAGE COMPOSITION OF	
	Clay substance.	Feldspathic detritus.
Silica	44.47	67.15
Alumina	39.79	19.03
Ferric oxid	0.32	1.00
Lime	0.07	0.66
Magnesia	0.02	0.22
Alkalis	2.75	11.95
Combined water	12.58	0.00
	100.00	100.00

Should the clay contain limestone detritus and appreciable amounts of uncombined ferric oxid or alumina, it is proper to extract these with dilute hydrochloric acid, and place them in the rational analysis by themselves. Similarly, if the clay contain soluble silica, this should be extracted, and added to the quartz.

When this is done, as before pointed out, the percentage formula of the "clay substance," as a rule, closely approximates kaolinite, the variation found from the latter being in the partial substitution of alumina by ferric oxid and of the combined water by alkalis and alkaline earths. These variations, however, the potter can easily learn to allow for, by the now simple comparison with the percentage composition of kaolinite.

It will occur to the chemist, that as the detritus of micas must be a constant constituent of clays, and as the dust of these minerals is practically all decomposable by sulfuric acid, and as their presence in the "clay sub-

stance" will vary its percentage composition just as described above, it would seem both justifiable and serviceable to assume that the alkalis and alkaline earths of the "clay substance" are contained in such combination, and using the average percentage of alkali in muscovite as a measure, deduct from each constituent a corresponding amount as going to make up so much mica.

The "rational analysis" of the above clay would, under this consideration, be

Clay substance	60.23 per cent.
Mica	23.89 "
Feldspar	9.04 "
Quartz	6.55 "
	99.71

the percentage composition being

	Clay substance.	Mica.	Feldspar.	Quartz.
Silica	43.75	46.30	67.15	100.00
Alumina	39.64	40.17	19.03	.....
Ferric oxid	....	1.13	1.00	.....
Lime	....	0.25	0.66	.....
Magnesia	....	0.08	0.22	.....
Alkalis	....	9.67	11.95	.....
Combined water	16.61	2.40	....	.....
	100.00	100.00	100.00	100.00

This extension of the "rational analysis" introduces a second hypothetical factor, which may often be justified in a primary clay where mineralogical examination confirms such a division, but beyond this, even the practical needs of the potter do not demand it, as the micas are not used as fluxes in ceramic industries, and their hypothetical presence would convey less meaning to him than the percentage composition of a "clay substance" easily comparable with kaolinite.

Clay analyses should always be calculated to the basis of the sample, dried at 120° C., as analyses showing varying amounts of moisture are not readily comparable. Upon the analyses of the other minerals, oxids, and salts used by the potter, it is not necessary to dwell. Especial impurities, for which it is alone necessary, often, to make examination, will be mentioned when the substances themselves are discussed.

Of ceramic products, the analysis of the pottery bodies is conducted similarly to that of a clay, care being taken in the preparation of the sample that every trace of glaze, etc., be chiseled or ground off. The calculation of the composition of a mass or paste for producing the same from known clays and minerals is readily done on well-known stoichiometric rules. A practical burning trial will then show how the mass obtained from the analysis will have to be modified to allow for the individual physical characteristics of the clays used.

The obtaining of samples of enamels and glazes from finished pieces of ware is often attended with considerable difficulty ; inasmuch as these are frequently very thin, or the body of the ware is so soft that it chips off with them, contaminating the sample.

The most practical way of obtaining them is to bed the piece from which the sample is to be obtained in clay, on a convenient table, surrounding the piece with large sheets of glazed paper, to catch the splinters of the glass as they are struck off. The enamel or glaze is now dressed off with small chisels of hardened steel, driven with a light hammer. As the chisels soon dull, a sufficient number

of them must be kept on hand to carry on the work. The blows of the hammer must be so regulated that the chisel does not cut into the body of the ware. When sufficient of the sample has been dressed off, it is carefully swept together with a camel's hair pencil, and probed with a bright, clean magnet until all the iron introduced by the chisels is extracted. It is then ground fine in the agate mortar for analysis.

From the usual components of potters' glazes, given in a later chapter, the chemist will understand what class of substances it is necessary to look for, and what precautions must be taken in the analyses. The almost constant presence of reducible metals would seem to make these analyses difficult, on account of the unavoidable fusions in platinum; but by unlocking the glasses with a liberal amount of alkali carbonate, and keeping the crucible well up in the flame, no reduction need be feared.

The frequent presence of considerable amounts of boracic acid in these silicates formerly presented an almost unsurmountable difficulty to accurate analysis, but Gooch's method of determining this substance[1] has overcome this trouble; yet we have still to deal with the most difficult phase of the determination, for the unlocking of boro-silicates containing frequently a very high percentage of reducible metal, compels fusion with large amounts of alkali, and the following acidification fills the retort with a great mass of troublesome salts.

[1] Bulletin of the U. S. Geological Survey, No. 42, p. 64. See also J. Anal. Appl. Chem., 2, 86.

CHAPTER II.

PHYSICAL AND EMPIRICAL TESTS.

HE physical properties of clays play so important a part in their use and in determining the character of the products which can be made from them, that the chemical analysis, by itself, is altogether insufficient to tell what qualities may be expected from such materials. Even in the matter of the color to be obtained on burning the clay, which would seem to hang most closely together with its chemical composition, the analysis leaves us, except in extreme cases and in a general way, in doubt.

The coloring of clays in the fire is due, primarily, to the presence of iron oxid, the tint being modified by the amount of lime occurring and influenced, occasionally by the presence of manganese, as also by the chemical quality of the flame during burning. But the depth of color of a burned clay is not at all in proportion to the contained iron oxid; a secondary clay may contain considerably less iron than a kaolin and yet burn quite yellow, while the latter burns snowy white. All depends upon the combinations in which the iron is held, and as long as we are unable to accurately separate the minerals of a clay, and subject them individually to examination, the chemical determination of the gross amounts of the

coloring oxids will give us but a very rough idea of the tints we may expect.

To formulate a systematic set of physical and empirical tests to characterize a clay is, on account of the widely differing needs of clay-workers, a very difficult thing. Yet obvious operations connected with its general use must be undertaken, and the conditions of the trials and their results must be described, as far as possible, in terms of physical and chemical measurement at common command. If this be done, inferences can be drawn from the experiments sufficiently close to the behavior of the clay under working conditions, to reliably forecast its serviceability or worthlessness for this or that purpose.

In this view, at least the following tests should be made:—

1. The fineness of grain of the constituents of the clay, measured by passing it dry or suspended in water through sieves of different mesh, or washing it with water at different measurable speeds of the wash-water, recording the proportion of each grade of fineness measured.

2. The plasticity, expressed numerically, by some measurable quality connected with it.

3. The binding property, given as tensile strength.

4. A firing under definite conditions of the chemical character of the flame, with record of the duration of the fire and the temperature reached, measured in a satisfactory pyrometric standard, to attain a specific hardness.

5. The porosity of the product burned as given, determined by its water-absorption.

6. The shrinkage from the clay state in which the material is formed to its burned condition.

7. Its coefficient of expansion, when burned as described, measured empirically by melting on it, at a heat lower than that of its original baking, a glaze of definite chemical composition, noting if in time, the glaze alone crack, a phenomenon called "crazing," or if it shatter the body or fly off at the edges, tearing the clay along with it, a phenomenon opposite to that of "crazing" and called "shivering," which result from either a too great or too small coefficient of expansion of the clay as compared with that of the glaze.

It is of course, quite important, that the sample for these physical and empirical tests be properly averaged, and in fact the same from which the portion for the chemical analysis is taken.

Much was hoped of the mechanical analysis of clays,[1] by clay-workers, in the direction of a serviceable separation of the material into its constituent minerals by their hydraulic values, as a preparation of the sample for chemical analysis and many separations were made with the apparatus of Schöne,[2] modified by Schütze.[3]

Disappointment at the results, in the light of the misapplied and over-great expectations has reduced this branch of operations to mere sieve-analysis and preparation of the sample for the analytical and physical tests of the clay, as the needs of the particular industry, in which it is likely to be used would indicate.

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[1] For an excellent discussion of the principles and methods see Wiley Principles and Practice of Agricultural Analysis, Vol. I, Part Fourth, p. 171.

[2] Zeitschrift für analytische Chemie, 7, 29.

[3] Notizblatt für Fabrikation von Ziegeln, etc., *1872*, 88.

The appearance, geological origin or a preliminary burning trial, giving the general use to which a clay may be put, the sample is prepared by passing it dry or more commonly by washing it through such a sieve as the mechanical preparation of the clay for the industry would demand.

The material remaining on the sieve used should be weighed and described. That passing through is dried and used for the various tests.

There is not, as yet, an altogether satisfactory measure of the plasticity of clays; though the possibility of giving direct numerical expression to this subtle and most valuable property would be of great practical value.

The best determination that can thus far be made is based on the observation that, in the main, the greater the plasticity of a clay the larger the amount of water required to bring it to a definite degree of softness, at which it can be worked.

In order to determine this point, apparatus have been devised for pushing, with a fixed load, a wire, rod or thin-walled cylinder to a certain depth and within a certain time, into the softened clay.

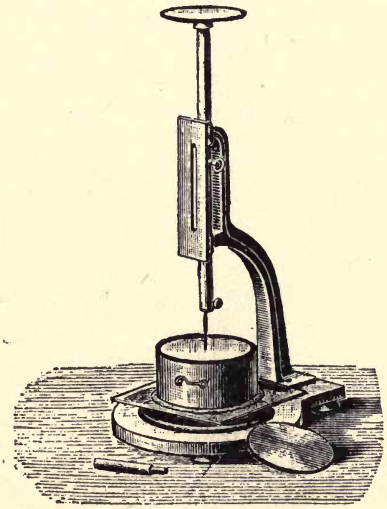
The proportion of water required to soften one hundred parts of the dry clay to the requisite emollescence is taken as the direct measure of the plasticity.

The apparatus necessary to determine, if the requisite softness of the clay is attained, which is most convenient, inasmuch as it is already in use for determining the time of setting of Portland cement, is Vicat's needle.[1]

[1] Transactions of the American Society of Civil Engineers, *1893*. Max Gary: The Testing of Portland Cement.

It has a wire of circular cross-section, the end cut at right angles to its axis, with an area of one square millimeter. The wire is over four centimeters long and attached to the end of a rod, suitably guided, which weighs 300 grams.

The softened clay is well "wedged" to make it perfectly homogeneous, and pressed into a ring four centimeters deep, set on a glass plate under the needle and struck off level with a steel spatula. The needle is then



VICAT'S NEEDLE.

allowed to penetrate the clay, and if within five minutes it sinks to a depth of four centimeters into the same, the clay is of the proper consistence; if not, it is either made stiffer or softened, as the case may be.

A weighed sample of the mass of proper consistence is dried and the proportion of water to 100 parts of dry clay is calculated, the figure being used as the direct index of the plasticity.

The binding power of clays is determined by tearing well-dried specimens formed in cement-briquette molds, the results being expressed in the weight in grams per square centimeter sufficient to break the clay.

Any of the standard machines for testing the tensile strength of cement[1] will answer the purpose.

It is necessary, however, to form the test briquettes very carefully, as they are liable to contain flaws, particularly with very plastic clays, which make it difficult to get concordant data.

The clay must be well "wedged" and beaten out into a slab rather thicker than the mold. By means of a bent tin stamp a piece of such dimensions, that it will very nearly fit the mold, is cut out, into which, after well oiling the latter and setting it on a dry plaster of Paris slab, it is beaten, and the excess of clay cut off with a thin wire. The mold is then slipped off the briquette, care being taken not to disturb its shape.

After the air-dried pieces have been broken in the machine, the surfaces of fracture must be measured before calculating the breaking load, that due allowance be given for the shrinkage of the clay in drying.

The binding power of clays is not necessarily proportional to their plasticity, as one would naturally sup-

[1] Journal of the American Chemical Society, 16, 161, *1894*. Thos. B. Stillman: The Chemical and Physical Examination of Portland Cement.

pose. The New Jersey ball clay described in a subsequent chapter is in striking illustration of this fact.

Clays which require a large amount of water to render them workable, and therefore show considerable shrinkage in the clay state, on drying, but which when dry are of low tensile strength, are liable to be very troublesome, particularly in the making of heavy and of dust-pressed wares by "checking," that is, showing surface cracks or "dunting" (cracking through). For drying, taking place from the surface of the piece, the material must be able to stand the strain of its shrinkage on a more slowly contracting center.

Where clays are deficient in this particular, great precautions have to be taken to prevent the loss of ware made with them in rapid drying, which often involves so much cost and care that the use of the material becomes out of the question.

Although half a dozen disks of the properly sampled clay, of the diameter and twice the thickness of a silver quarter, would answer to determine all that it is desired to know of the firing of a clay, this test cannot be made over a Bunsen or blast-flame, with the pieces packed in a platinum crucible, even with the help of the Erdman furnace; the difficulty being that with the simple appliances of the ordinary laboratory, it is not possible to get a sufficiently large zone in which the chemical character of the flame remains the same through a sufficient length of time, and in which the temperature is likewise the same and can be observed or measured without altering the conditions.

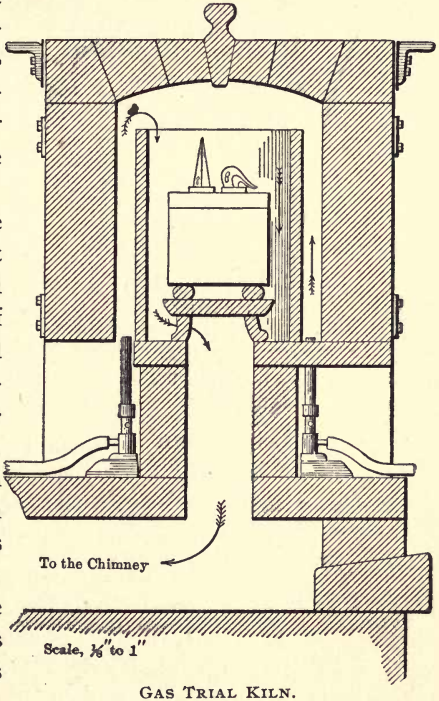
Hence it becomes necessary to make use of larger pieces of apparatus, which in the greater amount of time required in their heating, give a better opportunity, in the admission of fuel and regulation of the draft, to get the quality of flame desired, and further, by their slower and more regular advance in temperature, give the clay pieces, which are, in themselves, very poor conductors of heat, the opportunity of progressing in their entirety through the changes caused by advancing temperature, without a shrinkage of the periphery on the centers, causing distortion and unequal tension.

The ordinary assayer's muffle will answer the purpose of firing very well, whether it be heated with coke, gas, or gasoline; but the draught used should be the natural one of a good chimney, regulable by a damper and not the forced draught of a fan or bellows, as the quality of the flame is, in the latter case, too uncertain and difficult to regulate.

Where gas is available, the most convenient furnace is one made after designs of Seger, by Geith, in Coburg, Germany, consisting of a ring of eight Bunsen burners, the flames playing into a fire-clay furnace and forced by the connection with the chimney in the bottom, to play over a ring and down on the crucible or "saggar" before passing into the flue. In this way, by the up and down passage of the flame, a large zone of uniform temperature is well attained. The arrangement will be well understood from the sketch of a similar contrivance which can easily be extemporized with good fire-brick and tile by a practical brick-layer.

For attaining high heats, it is, of course, imperative that the gas pressure be sufficient, a condition often only to be had in the evening, as most of our gas companies are conducted.

The temperature at which different clays should be fired and the melting of glazes on the fired pieces, to empirically test their coefficients of expansion, can best be explained in connection with the considerations applying to their use, and is deferred to the respective chapters on the different wares as the results of experimental burning are only of value when looking to the conditions of definite products, and when the heats to which the trials have been subjected are measurable and can be reproduced and controlled, to a similar degree, in the kilns of the potter. The subject of pyrometry becomes one of the greatest importance in this connection; to it, the subsequent chapter will be devoted.



GAS TRIAL KILN.

In the case of clays intended for making floor-tile and paving-brick, and for ware which is to be partly glazed and exposed to the influences of the weather, it is important to know how porous it still is after receiving the proper fire. It is sufficient, for this purpose, to determine the weight of water that the burned specimen will absorb.

In making the test it is important not to immerse the entire piece in water, as this would seal the pores and make it very difficult to get rid of the air in the interior. One face of the specimen must be left dry, and the water allowed to rise by capillarity, the piece not being lowered under the surface of the water until all its air has been expelled. It is superficially wiped off before weighing.

As all clays shrink in the fire, but show the greatest variation in this property, and as articles made from them are generally required to come to definite sizes, hollow-ware being made to certain capacities, sanitary-ware having to fit metallic fittings, and brick and tile being required of standard sizes, a description of the physical properties of a clay involves a statement of the amount of its shrinkage from the plastic condition in which it is worked to the condition reached at the temperature in which it is burned; so that from it the artisan will be enabled to calculate the sizes of his molds or dies.

If, for the burning trials, disks of about one and one-half inches in diameter and three-sixteenths of an inch thick, be beaten out from the plastic clay on clean bats of plaster of Paris, the surface of the disks being smoothed with a knife or steel spatula and two dots impressed or

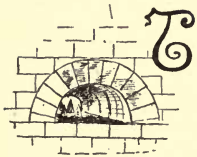
lines drawn into the soft clay, just twenty-five millimeters apart, the shrinkage of the clay is found with sufficient accuracy after the trials have been burned, as in the second measurement, quarter millimeters are easily estimated so that the result may be given in per cents.

Articles of which the greatest precision in size is required, flooring and wall-tile and fine pressed brick, are not formed from clay in the plastic state, but from fine clay-dust containing from eight to twelve per cent. moisture, so that it just packs when squeezed between the fingers.

The shrinkage of the dust-pressed and plastic-pressed clay will vary somewhat, and it is useful to make for the burning a few dust-pressed disks, beside the plastic ones. This is easily done in a large diamond mortar, twenty-five millimeters in diameter. It must be well cleaned and oiled, the ring filled one-third to one-half full of the slightly dampened clay-dust, the pestle inserted and pushed down, then struck twice gently with the hammer in order to pack the clay, but still let out the air, and finally struck two sharp blows with the hammer to compress and seal the disk. It is then carefully pushed out, and after being dried and fired to the established heat, is measured to quarter millimeters with a pair of calipers and the shrinkage recorded in per cents.

CHAPTER III.

PYROMETRY.



THE subject of pyrometry is one of the most vital interest to an industry making use of the greatest range of high temperatures, and risking large quantities of ware to an operation which will make or mar it, unless the heat desired be attained within a very narrow range of variation.

Potters use, for their guidance in determining if the requisite high temperatures have been reached, empiric trial-pieces made of materials used in their manufacture, the behavior of which in the fire they have become familiar with in the course of their practical experience. Such trial-pieces are usually rings of clay or shards of baked clay coated with glaze mixtures, fusible clay, or feldspar.

Usually these empiric standards serve their purpose very well in the hands of experienced men, though they fail at times, even under such use, through mechanical and chemical changes of the materials, which nothing but careful analyses would detect and which are usually not made.

It will be appreciated that the personal factor is a very great one in the judging of such empiric pyrometric trials,

and it is this that the burner of better classes of ware, particularly, turns to his account, in making himself indispensable to a manufacturer, who is loth to entrust the dangerous operation of burning to one who has first to make his experience with the trials.

But even in the hands of the experienced burner, they have the disadvantage that they do not enable him, except in a very imperfect way, to strike other temperatures with which he has not previously worked. He is therefore helpless under all but the limited conditions of his immediate experience.

As the trials of different establishments bear no relation to each other, their experiences in firing are not comparable, and they cannot be mutually helpful, even when there is an entirely cordial disposition to be so.

As the first principles of systematic chemical investigation involve the use of standards that are comparable and easily attained, it would be useless to go into the present practical kiln trials of our potters beyond mentioning them in connection with the different classes of manufactures, which will be done in the appropriate places.

It is necessary, however, to carefully consider the conditions imposed upon pyrometric observations in pottery kilns, in order to select the best means, of those proposed, for making them.

The first and most obvious condition is that the pyrometer should be of such positive action that there enter no personal factor into its reading. That while it be sufficiently wide in range to cover all temperatures of

ceramic operation, the divisions must be so close that the progress of physical change of clays and glazes made in the fire be not beyond the observable progress of the pyrometer.

These obvious conditions rule out all optical pyrometers which have thus far been made.

Furthermore, kiln-men, even if they be teachable, have to do rough work, and cannot be expected to manipulate delicate instruments with hands roughened and sense of touch blunted by coal-shoveling.

Pottery kilns are large affairs, having commonly an internal diameter of sixteen feet and a height of fourteen feet. The heat, proceeding from a number of fires, can only be made to progress uniformly, by observation at a number of points, which are seldom less than four, and generally about eight. These points must be average ones, as far as temperature conditions are concerned, and can hardly be nearer than from four to six feet to the outer circumference of the kiln. Pyrometers whose indications must be transmitted through this distance of widely varying temperatures in order to be read on the outside are difficult to place, and their readings become complicated with correcting factors that are hard to fix.

If the expense of the appliance be such that one cannot be left in each place of observation, but one or two instruments must be used to make all the measurements of perhaps several kilns; the length of time consumed in the work will be such that at the critical time all necessary observations and regulation of the fire by them cannot be made with sufficient expedition; for upon open-

ing the kiln for the introduction of the instrument, the invariable suction of a strong draught of cold air to the point where it is to be placed results and so far cools that locality that some time must elapse, after all has again been made tight, before a reading can be taken.

Another consideration, inherent in almost all conditions where pyrometric determinations become desirable, is very frequently lost sight of; namely, that heat is required to do work in a body which, through its mass or poor conductivity, responds but slowly to the impact of the flashes of the former. Through this comparatively slow response, the body averages within itself the effect of heat waves of widely differing temperatures which it is constantly receiving.

Now, a pyrometer which is not similarly capable of averaging the heat impressions received will be too sensitive; many readings will have to be made in order to get the average, or these will have to be recorded as a curve, by a suitable instrument. The former occupies too much time; the latter involves the exposure of a delicate mechanism to places and conditions that are very destructive to it.

One fact has done much to retard real progress in pyrometry; namely, the fundamental association, in most minds, of the thermometric degrees of the mercury thermometer as something inseparable from all temperature measurements.

The great utility of using the expansion of liquids, where the range of temperature makes it admissible, accounts for this very natural error. But even in cer-

amics, where, perhaps, the greatest range of heat requiring exact control is used, not self-regulable as is, to a certain extent, the case in many chemical and metallurgical processes, there is no occasion to pass from the thermometric scale to higher heats by a regularly graduated system, and the attempts to extend, by calculation and interpolation by over 2,000°, a system which gives data for less than 400, have awakened false and unattainable aims.

The connecting of pyrometric with the common thermometric system can, and, in any case, must be done by the calorimeter; but the former need not, therefore, and should not be divided by thermometric degrees.

The difficulties of pyrometry and the varying conditions under which it must be executed may make instruments based on a variety of manifestations of physical change, varying positively under increasing heat necessary. The expansion of gases, the decreasing electrical conductivity of metallic circuits, the melting down of pyroscopes of progressive variation in chemical composition, may all be successfully employed for the purpose in different places, but only the latter have maintained the promise of permanent success under the difficult conditions of ceramic pyrometry, as enumerated.

The first of such melting pyroscopes that gave good service and can still be employed under proper precautions and in certain range, are the metals silver and gold and their alloys, and the alloys of gold with platinum, as suggested by Prinsep.[1]

[1] Philosophical Transactions, *1828*, p 79.

These are made by weighing off accurately the relative proportions of the pure metals, in the form of wire, and then combining the portions by thorough fusion before the blowpipe. The alloy beads are hammered to flat disks, the melting of which is easily observed by their collapsing and drawing into the bead-form. The alloys usually used are the following: their melting-points were determined by Erhard and Schertel.[1]

Percentages.		Melting-point.	Percentages.		Melting-point.
Gold.	Silver.		Gold.	Platinum.	
00	100	954°C.	95	5	1100°C.
20	80	975	90	10	1130
40	60	995	85	15	1160
60	40	1020	80	20	1190
80	20	1045			
100	00	1075			

On account of the difficulty, however, of obtaining amounts of alloys of absolutely uniform composition, these can only be used in small plates one or two decigrams in weight, which are not observable at any distance, particularly not in luminous surroundings, and require their extraction from the places of exposure for observation. Furthermore, on account of their becoming crystalline in a very slowly rising heat, and the leaching out from the crystalline mass of drops virtually different in composition and melting-point from those of the entire alloy, it is not possible to leave a number of them in the kiln and withdraw them one by one with the rise in heat, for purposes of observation, but they must be introduced when the heat is suspected to be near the

[1] Jahrbuch für das Berg-und Huttenwesen in Sachsen, *1879*.

point wished, remain until they have the full heat of the surroundings, and then be withdrawn for observation. This makes too much manipulation for practical work, and the small alloy plates are frequently lost, entailing, on account of their cost, considerable expense.

The difficulty of the changing physical character of the gold platinum alloys is particularly troublesome when the latter metal amounts to twenty per cent. and over, so that considerable uncertainty attaches to the tests at higher temperatures.

The advantages of the Prinsep alloys as bodies practically uninfluenced by oxidizing or reducing atmospheres, melting down at regular sufficiently close intervals, suggested to Dr. Heintz[1] the adoption of glass mixtures on the type of porcelain glazes, for the same purpose. Their cheapness, the possibility of forming them into masses easily observed without withdrawal from the place of exposure, rendered them suitable for the purpose.

The chief problem became the making of as great a range of them as possible without the introduction of reducible elements, and to make the composition such as to obviate all danger of their undergoing, on long exposure, a crystalline change or devitrification which would alter or disturb their certain melting down, the condition in which the ultimate value of a large part of the series of Prinsep's alloys failed.

This problem was undertaken by Seger,[2] and solved

1 Thonindustrie-Zeitung, *1886*, p. 135.

2 Thonindustrie-Zeitung, *1886*, pp. 135, 145, 168.

so successfully that his "Normal Pyrometric Cones" answer all conditions required in ceramic pyrometry.

He established that the most fusible mixture of the porcelain glaze type was one of the chemical composition:

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} 0.5Al_2O_3 4SiO_2.^{1}$$

From this the more infusible glasses were obtained by the systematic increase of silica, with a proportional increase of alumina to correct the well-known tendency toward devitrification of highly siliceous glasses.

By the partial substitution of alumina with ferric oxid, the series was brought down, in its member,

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} \left.\begin{matrix} 0.3\ Al_2O_3 \\ 0.2\ Fe_2O_3 \end{matrix}\right\} 4SiO_2,$$

to equal the melting point of the alloy ten per cent. platinum, ninety per cent. gold, and thus became continuous with the most useful members of Prinsep's series.

The use of the cones proved to be so practical for the purpose that the need to substitute the Prinsep alloys by equivalent cones was soon felt, and E. Cramer,[2] making use of the well-known fact that if the acidity of a glass be maintained, but the silica substituted by boracic acid, the melting-point is lowered, increased the series to begin with the melting-point of silver.

These pyrometers are, in the entire range demanded by ceramic firings, represented in the following list.

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1 Thonindustrie-Zeitung, *1886*, p. 168.

2 Thonindustrie-Zeitung, *1892*, p. 155.

For the benefit of those who find it difficult to free themselves from the association of thermometric degrees with advances in heat, such degrees have been interpolated, from calorimetric determinations, as follows:

Cone 010, melting down with pure silver, 960° Celsius; cone 1, melting with the alloy ninety per cent. gold, ten per cent. platinum, 1150° Celsius; cone 20, 1700° Celsius.

Cone number.	Chemical Composition.				Estimated temperature in degrees Celsius.
010	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.50SiO_2$ $0.50B_2O_3$		960
09	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.55SiO_2$ $0.45B_2O_3$		979
08	$0.3K_2O$ $0.7CaO$	$0.2FeO_3$ $0.3Al_2O_3$	$3.60SiO_2$ $0.40B_2O_3$		998
07	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.65SiO_2$ $0.35B_2O_3$		1017
06	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.70SiO_2$ $0.30B_2O_3$		1036
05	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.75SiO_2$ $0.25B_2O_3$		1055
04	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.80SiO_2$ $0.20B_2O_3$		1074
03	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.85SiO_2$ $0.15B_2O_3$		1093
02	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.90SiO_2$ $0.10B_2O_3$		1112
01	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$	$3.95SiO_2$ $0.05B_2O_3$		1131
1	$0.3K_2O$ $0.7CaO$	$0.2Fe_2O_3$ $0.3Al_2O_3$		$4SiO_2$	1150
2	$0.3K_2O$ $0.7CaO$	$0.1Fe_2O_3$ $0.4Al_2O_3$		$4SiO_2$	1179
3	$0.3K_2O$ $0.7CaO$	$0.05Fe_2O_3$ $0.45Al_2O_3$		$4SiO_2$	1208
4	$0.3K_2O$ $0.7CaO$	$0.5Al_2O_3$		$4SiO_2$	1237

Cone number.	Chemical composition.	Estimated temperature in degrees Celsius.
5	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{0.5Al_2O_3\right\}5SiO_2$	1266
6	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{0.6Al_2O_3\right\}6SiO_2$	1295
7	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{0.7Al_2O_3\right\}7SiO_2$	1323
8	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{0.8Al_2O_3\right\}8SiO_2$	1352
9	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{0.9Al_2O_3\right\}9SiO_2$	1381
10	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{1.0Al_2O_3\right\}10SiO_2$	1410
11	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{1.2Al_2O_3\right\}12SiO_2$	1439
12	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{1.4Al_2O_3\right\}14SiO_2$	1468
13	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{1.6Al_2O_3\right\}16SiO_2$	1497
14	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{1.8Al_2O_3\right\}18SiO_2$	1526
15	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{2.1Al_2O_3\right\}21SiO_2$	1555
16	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{2.4Al_2O_3\right\}24SiO_2$	1584
17	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{2.7Al_2O_3\right\}27SiO_2$	1613
18	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{3.1Al_2O_3\right\}31SiO_2$	1642
19	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{3.5Al_2O_3\right\}35SiO_2$	1671
20	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\}\left\{3.9Al_2O_3\right\}39SiO_2$	1700[1]

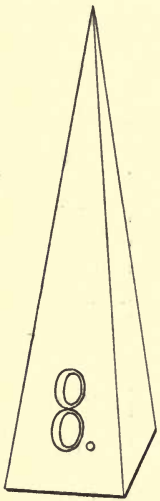
In order to secure for these pyrometric mixtures a standard character, and justify the name, "Normal

[1] Thonindustrie-Zeitung, No. 49, *1893*, p. 1252–3.

Pyrometric Cones," they are manufactured by the Prussian Government in their ceramic experiment station at the Royal Porcelain Works, in Charlottenburg, near Berlin.

It is, however, not at all difficult to make them of sufficient accuracy, from the excellent native materials that are on the market in the United States.

Thus the original series of Dr. Seger are made as follows: The potash is taken in the form of orthoclase; the remaining alumina that is requisite is introduced in the form of kaolinite; and the remaining silica, not supplied by these, is added as quartz. Calcium carbonate gives the calcium oxid, and those needing ferric oxid have it directly added.



A SEGER CONE IN NATURAL SIZE.

The necessary amounts of these ingredients are weighed off for each number, introduced with water into a small porcelain jar mill, thoroughly ground for half a day, settled, the water drawn off, and the mixture dried. It is then worked into a mass with dextrin mucilage, and formed into tetrahedrons six centimeters high and one and one-half centimeters on the sides of the triangular base.[1]

The materials selected by Dr. Seger as sufficiently pure for the purpose analyzed as follows:

[1] Thonindustrie-Zeitung, *1886*, p. 136.

	Rörstrand feldspar. Per cent.	Zettlitz kaolin. Per cent.	Norwegian quartz. Per cent.	Carrara marble. Per cent.
Silica	64.32	46.87	98.52	1.00
Alumina	19.41	38.56	1.04	
Ferric oxid	0.14	0.83	0.04	0.12
Lime	trace	trace	....	54.93
Magnesia	0.35	trace	....	0.20
Potash	12.90	.06	0.40	....
Soda	2.10		....	....
Loss on glow'g	0.57	12.73	....	....
Carbon dioxid	....	....	....	43.76
	99.74	100.05	100.00	100.02

One can make with the raw materials produced and put on the market in this country quite as near an approach to the theoretical figures, and need, therefore, have no hesitancy in using them for such a purpose. The following analyses will verify this fact:

Kaolin, from Western North Carolina, of which the writer has made over fifty analyses, not varying materially from the following extremes:

	Analyzed November, 1890.	January, 1894.
Silica	46.47	46.67
Alumina	38.82	38.14
Ferric oxid	0.89	0.36
Lime	0.28	0.50
Magnesia	0.25	0.09
Potash	0.63	0.64
Soda	0.12	
Combined water	03.34	13.61
	100.53	100.11

Feldspar from New York:

	Per cent.
Silica	65.85
Alumina	19.32
Ferric oxid	0.24
Lime	0.56
Magnesia	0.08
Alkalies[1]	14.10
	100.15

Quartz from Illinois:

Alumina	0.155
Ferric oxid	0.069
Lime	0.026
Magnesia	0.013
Alkalies	0.112
Total impurities	0.375
Silica (by difference)	99.625
	100.000

Commercial Whiting:

Silica	trace
Alumina, Ferric oxid	0.13
Magnesia	trace

In order to make cone No. 1, having the formula

$$\left.\begin{matrix} 0.3K_2O \\ 0.7CaO \end{matrix}\right\} \left.\begin{matrix} 0.2Fe_2O_3 \\ 0.3Al_2O_3 \end{matrix}\right\} 4SiO_2$$

there would be ground together and formed into tetrahedrons, as described,

0.3 equivalents		feldspar	83.55 parts.
0.7	"	calcium carbonate	35.00 "
2.2	"	quartz	66.00 "
0.2	"	ferric oxid	16.00 "

[1] Combining weight, 45.9.

For cone No. 4, having the formula

$$\left.\begin{matrix} 0.3K_2O \\ 0.7CaO \end{matrix}\right\} 0.5Al_2O_3.4SiO_2.$$

there would be used

0.3	equivalents	feldspar	83.55
0.7	"	calcium carbonate	35.00
0.2	"	kaolinite	25.90
1.8	"	quartz	54.00

For cone No. 10, having the formula

$$\left.\begin{matrix} 0.3K_2O \\ 0.7CaO \end{matrix}\right\} 1Al_2O_3.10SiO_2.$$

there would be used

0.3	equivalents	feldspar	83.55
0.7	"	calcium carbonate	35.00
0.7	"	kaolinite	90.65
6.8	"	quartz	204.00

For the introduction of boracic acid into the lower scale, according to E. Cramer this element is first fixed as a lime-soda glass of the composition

$$\left.\begin{matrix} 0.5Na_2O \\ 0.5CaO \end{matrix}\right\} 0.2Al_2O_3 \left\{\begin{matrix} 2SiO_2. \\ 1B_2O_3. \end{matrix}\right.$$

by melting together

191	parts	crystallized borax.
50	"	calcium carbonate.
52	"	kaolinite.
96	"	quartz.

Then equivalent amounts of this glass are ground with equivalent amounts of feldspar, kaolinite, quarz, calcium carbonate, and ferric oxid, to make bodies of the corres-

ponding formulas, and the masses are formed into tetrahedrons, as described before.

The use of the Seger cones is very simple. One of the number, representing the heat which it is wished to reach, is set upright in each of the proper places of the kiln opposite a spy-hole, which latter is closed with a plate of mica. When, by the advancing heat, the cone bends until, finally, its apex touches the base on which it is set, the temperature which it is intended to indicate is reached, and the firing stopped.

The cones should be set about three feet back from the kiln-wall, in a piece of fire-clay piping or muffle extending to the kiln-wall and running a foot or more back of the pyrometer, so that this is seen, when the fire is well advanced, as a luminous body in a darker field. The pyrometer is best stuck with a little soft mud on a fire-clay shard or tile, to prevent its falling over.

The determination of the proper pyrometer to be used as the index of the heat to which a clay under examination should be burned is best explained in connection with the examination of clays for specific industries, and is deferred to these chapters.

CHAPTER IV.

CLASSIFICATION OF CERAMICS.

A GENERAL classification of clay manufactures will be of service in this connection, particularly to the chemist, who may not, heretofore, have given much consideration to ceramics, in order to emphasize characteristics that are of moment to the potter.

The varieties of ware manufactured in the United States are not very great, and can be quite sharply characterized. It will therefore be most practical to take as simple a classification as possible, especially as it is mainly made for the benefit of the technical chemist, and not for the connoisseur, and need merely enumerate the chief technical characteristics without classifying all their possible combinations.

The old classification of Brogniart is accordingly taken as a basis for the purpose.

He divides all ceramic products into three main classes and nine subdivisions, as follows :

First Class.—Bodies sufficiently soft to be scratched with a knife, of a sandy-argillaceous character or containing lime and fusible in the heat of the porcelain kiln.

First Division.—Bodies soft burned, with a dull unglazed surface. Examples : Brick, building terra-cotta, drain tile, etc.

Second Division.—With the faint luster of an alkali-earthy-silicate, the gloss produced by polishing or by incipient fusion. Example: Antique vessels.

Third Division—A body similar to that of the first or second, but with a transparent lead glaze. Example: Common pottery ware.

Fourth Division.—Ware enameled with nontransparent glazes containing tin oxid. Examples: Tile for porcelain stoves, and common dishes.

SECOND CLASS.—Bodies that are hard, nontransparent, of a siliceous-argillaceous mass that cannot be scratched with a knife, and are infusible.

Fifth Division.—White body with a transparent lead glaze. Examples: Fine faience and dish-ware.

Sixth Division.—A colored body with an earthy alkaline silicate glaze, or sufficiently dense to require no glaze. Example: Stoneware.

THIRD CLASS.—Bodies hard, translucent, high in alkali, siliceous-argillaceous, softening in the hardest fire.

Seventh Division.—Kaolinitic body with a glaze mainly feldspathic. Example: True hard porcelain.

Eighth Division.—Body of kaolin, plastic clay, and bone ash, with a lead-boracic-acid glaze. Example: English soft porcelain.

Ninth Division.—Body of a glass-frit with addition of clay and a lead glaze. Example: French soft porcelain.

In addition to the manufactures innumerated by Brogniart in his first division, flooring tile would belong in

this category. It is now, however, customary to burn these, as well as the better grades of building terra-cottas, so hard that they are not to be scratched with a knife; enabling them to better resist wear and the disintegrating action of the elements.

Our common "red ware" corresponds exactly to that of the third division.

In the fourth division, the only representatives of American ware are white enameled brick. Occasionally dishes are brought to the New England coast towns from Fayal, in the Azores, corresponding exactly to those described by Brogniart; but clays rich in lime, such as the tin enamels melt best on, are only used with us in the manufacture of cream-colored brick—not for dishes; and tin-enamels, apart from their employment on brick, have only been employed on metal vessels.

Our common dishes, better in grade than red ware, are made in yellow and Rockingham ware, which should come under the second class, in having a hard siliceous-argillaceous body that cannot be cut with a knife, and is porous and opaque. There is no division, however, into which it will exactly fit, for the body is yellow and the glaze transparent and plumbiferous, and, in the case of Rockingham ware, manganiferous.

All enumerated varieties of ware of the fifth division are common with us, and are variously termed cream-colored ware ("C. C."), white granite ware ("W. G.")' ivory white ware, ironstone china, etc.

Similarly, all classes of the sixth division are common in the United States, the stoneware being commonly

divided into "salt-glazed" and "slip-glazed" products, the meaning of which terms will be explained in the chapter devoted to these wares.

The paving-brick now extensively manufactured in the United States come under the unglazed products of this category.

The wares thus far enumerated are called in English, collectively, "pottery," and it is with the chemical character of these, particularly with the glazed varieties, that this book, in the main, concerns itself.

Those coming under the third class have, within recent years, begun to be manufactured in quantities assuming proportions of commercial importance, with the exception of the French pâte tendre, which is not made.

We have, however, a kind of ware standing between that of the fifth division and porcelain, for which there is in this classification no exact place. It is commonly known as "hotel china," and resembles porcelain in having a vitreous body, rich in alkali, that in thin places would be translucent, but which is covered, like the ware of the fifth division, with a clear lead glaze.

There is one misnomer in popular use that may cause the chemist looking up the proper significance of the term some misunderstanding; namely, the word "Majolica." In the United States, it is commercially a cheap ornamental ware, with a white, rather soft body, decorated with designs in relief, and these designs tinted with soft, transparent, colored glazes.

Originally, the term was applied by the Italians of

the fifteenth and sixteenth century to white enameled ware decorated in lusters—that is, in colors having a metallic reflex—which was, at first, of Moorish make, and brought to Italy, largely from the island of Majorca and afterward it was applied to all ornamented white enameled ware ; ware belonging, however, in all cases, to the fourth division of Brogniart.

The word faience is also one commonly misunderstood. Originally, it meant majolica from the potteries of Faenza, but finally became synonymous with majolica in general, meaning an ornamented white ware. But the name was most commonly used in France, where white ware, made with white clays and a transparent plumbiferous glaze, largely took the place, both in ornamental and useful articles, of the white tin-enameled pottery ; so that the term lost its specific meaning, and came to mean pottery of a little better grade in general.

Ceramists are inclined now to use the term "faience" in distinction from the application of the word "majolica," using it to designate potteries with transparent glazes, and majolica, as a generic term for potteries with intransparent glazes.

In this sense, our potters are already using the word faience quite correctly for ornamented wares belonging both to the third and fifth division of Brogniart.

It is to be hoped that our incorrect application of the word majolica, which is only used as a trade name for an inferior grade of ornamental ware, will sink with the latter into obloquy.

The word "enamel" has attained a specific signifi-

cance which the public frequently misapplies, using it indiscriminately for all glazes or glassy coverings.

Technically, the word enamel means an nontransparent glass, completely covering the body upon which it is melted, the nontransparency being due to the presence of tin oxid, arsenic, bone ash, or cryolite.

It is important that the technical significance be adhered to, and that the indiscriminate popular use of the word be realized, to prevent misunderstandings.

Ceramic wares pass into each other by almost imperceptible gradations. The great variety of possible bodies, glazes, decorations, means of shaping, applications, opens an almost infinite field to the fancy of the worker and the greatest number of combinations to meet specific uses.

It is an error to suppose that the so-called finer grades of ceramics, though made of pure kaolin, feldspar, and quartz, and white-burning secondary clays, alone offer artistic possibilities or problems worthy of the chemist's consideration.

On the contrary, the wares that have brought us the interest of foreign countries belong to the first, third, and sixth division of Brogniart's classification; they represent the largest commercial factor in our clay industries, and in their midst the greatest artistic success has been achieved.

While we are better supplied with pure pottery materials than any other country, our common clays will, and properly should, always claim the greatest share of interest, not only because they must be the raw mate-

rials of the bulkiest manufactures, and those in which the greatest economies will have to be exercised, but because they will always offer the greatest technical and artistic possibilities.

CHAPTER V.

POTTERY GLAZES.

S EXPLAINED in the previous chapter, pottery bodies have, in the main, an earthy fracture, and even when sufficiently hard so as not to be scratched with a steel point, may absorb fifteen to twenty per cent. of their volume of liquid, with avidity. But even vitreous bodies that were very brittle, and had a conchoidal glassy fracture, were found by the writer to absorb up to one and eight-tenths per cent. of their weight, or nearly four per cent. of their bulk, of distilled water.

From this it will be seen that all pottery and porcelain articles, if they are to serve as containers or be subject to conditions making frequent cleaning necessary, should be covered with an impervious surface coating. This is practically always a glass.

The glass, or "glaze," as it is designated, must necessarily answer the following conditions:

(1) It must have practically the same coefficient of expansion as the body of the ware, in order not to "craze"; that is, tear with transverse cracks; or not to push off on high places and sharp angles, tearing the body along with it, called "shivering."

(2) It must bear exposure in thin layers to gradually

increasing temperatures, lasting hours, or even days, during baking, without suffering devitrification.

(3) It must be sufficiently tenaceous when melted so as not, in the necessarily long time in which it is in this state, to run off of upright objects, nor yet so stiff as not to flow perfectly smooth on flat ones.

(4) It must hold dissolved, without unsightly separations, metallic oxids that have been added for imparting color.

(5) It must not exert too strong a solvent action upon oxids used in painting and printing upon the body of the ware, over which the glass is afterward melted like a covering of indestructible varnish.

The difficulties attending the fulfilling of these general conditions, besides many special ones that occur in connection with every kind of ware, have naturally led potters to guard the composition of those that answered their particular purposes with great jealousy.

The formulas that have been published are, in the main, misleading, or, where this is not the case, they are, as a rule, equally useless, inasmuch as the interdependence of glaze, clay, and the condition of firing is so intimate that even a correct description of one, without the others in conjunction, is of no practical service.

It is furthermore impossible to judge *a priori* of what may be expected of a glaze in melting-point, coefficient of expansion, and tendency toward devitrification from its gross composition by weight. This must be resolved into the chemical formula, and in order to do this, the chemical character of the compound and the function of its elements must first be understood.

The practical experience of the potter teaches him that he needs as a glaze a body resembling in hardness, color, and refracting power ordinary flint glass; but that ground flint glass, painted on his ware and exposed in the kiln, will not, under any circumstance, give him a glaze having the qualities the glass before, in itself, had, but a puckered, devitrified mass, barely sintered together.

To whatever circumstance this may be due, he knows still that what he needs is a glass or a mixture composed of the elements of a glass, which, to meet his special purposes, can be modified in the following ways.

To reduce the melting point, the alkalies, alkaline earths, and certain oxides of the heavy metals, particularly and almost indispensably lead, must be increased; that with this increase and resulting greater fusibility, the glaze becomes more brilliant; that is, attains a higher refractive index; but will inevitably craze if the increase of these bases exceeds a certain amount.

Conversely, to counteract the crazing of the more fusible glazes on certain clays, the addition of quartz to the glaze corrects this defect, with attendantly growing difficult fusibility, until, finally, the coefficient of expansion is so far changed that the glaze tends to push off from the body at elevated places and angles, and this increase of quartz may be pushed to the extent that the glaze will shatter the entire piece of ware which, as already said, is called "shivering." These are the extremes between which the proportion of base and acid must lie.

The action of boracic acid is similar to that of the quartz or silica in changing the coefficient of expansion,

in opposition to the effect of the bases, but the melting-point does not rise in the same proportion. On the contrary, by the substitution of silica with boracic acid, the melting point falls very materially. The glaze also increases in brilliancy with this addition, but is softer, being more easily scratched, and exerts a far greater solvent action on under-glaze colors.

Glazes composed of the above constituents, while they seem to answer every requirement when melted in the experimental muffle, fail utterly when used in the large ware kiln. The potter has found empirically that no glaze can be perfect without the addition in certain proportion, of either clay, feldspar, or Cornwall stone, and the chemist will readily recognize that the new element introduced by these materials is merely alumina, and that it is this and other chemically similar elements which keep the glaze from devitrification in the protracted "glost-fire" of the potter's oven.

In calculating the chemical formula of glazes, the bases, with the exception of those of the alumina group, are reduced to their equivalent proportions, and multiplied by such a factor that their sum equals unity. The corresponding equivalent weights of the members of the alumina group are then recorded together, as they occupy an intermediary position, in fixing the relations of the bases to the acids, under protracted firing, and then the equivalent weights of the acids are noted.

A glaze would then have the formula $10\,RO\,x.\,R_2O_3\,y.\,SiO_2$.

A common flint bottle-glass was found to have the composition:

Soda	17.80	per cent.
Lime	6.37	" "
Magnesia	2.83	" "
Alumina	0.53	" "
Silica (by difference)	72.47	" "
	100.00	

the chemical formula being

$$\left.\begin{matrix} 0.61\ Na_2O \\ 0.24\ CaO \\ 0.15\ MgO \\ 1.0\ RO. \end{matrix}\right\} 2.56\ SiO_2.$$

Finely ground and applied to a burnt shard of clay, it was scarcely possible to get with it a bright transparent glaze in the experimental muffle.

By taking a half equivalent of the glass and one-half equivalent of a lead compound, and making up the silica by addition of ground flint, as follows:

$$0.5 \text{ equivalent of the glass} \left\{\begin{matrix} 0.305\ Na_2O \\ 0.120\ CaO \\ 0.075\ MgO \end{matrix}\right\} 1.28\ SiO_2$$

$$\begin{matrix} 0.5 & PbO & 1.28\ SiO_2 \\ \hline 1.0 & & 2.56 \end{matrix}$$

made by thoroughly mixing in a mortar with water 52.71 flint glass, 55.75 litharge, and 38.4 flint; and painting the mixture on a potsherd, it flowed to a brilliant glaze at a temperature above that of the melting point of an alloy, fifty per cent. silver and fifty per cent. gold.

In the potter's glost-kiln, under a thirty hours' fire and two days' cooling, the glaze was puckered and dull.

The introduction of two-tenths equivalents of alumina, in the form of china clay, with allowance for the silica necessarily introduced with it, corrected it for these conditions so that the glass, composed of

0.5	equivalent	flint glass,	52.71	parts,
0.5	"	litharge,	55.75	"
0.2	"	china clay,	25.9	"
0.88	"	flint,	26.4	"

answered on a shard of the proper coefficient of expansion, and came brilliant and clear from the long fire.

This example, illustrating the functions of the different elements composing a glaze, sufficiently explains the structure of the chemical formula and the insight it gives one into a complicated glaze formula.

It must not be inferred from the above, however, that a flint glass should be the basis of every pottery glaze, nor that every glaze must contain lead.

Potters are accustomed to distinguish between "raw" and "fritted" glazes. The former have merely their constituents ground together and are melted to a glass for the first time when exposed on the ware to the glost-fire.

Fritted glazes are those that contain a glass or, rarely, are such as have been entirely melted to a glass before grinding and putting on the ware.

The purpose of fritting all or a part of the constituents of a glaze is primarily to render insoluble such constituents as would, by their solution in water, be carried away by the customary wet-grinding and the application of the glaze, suspended in water, to the ware. This is the

case when soda-ash, pearl-ash, borax, niter, boracic acid, and similar constituents are to be incorporated in the glaze. At times, too, when a glaze contains large amounts of alkaline earths, with little or no lead oxid, fritting is necessary, as the alkaline earths, not being in themselves fusible, enter with difficulty into combination, and would require, for the incipient union, heats far too excessive for the glass when actually formed.

In order to illustrate the calculation of the formula of a glaze from its analysis, the following example will serve. The sample was taken from a plain-glazed tile of American manufacture, as explained in the first chapter, and gave the following percentage composition:

Lead oxid	24.21 per cent.
Alumina	11.58 " "
Silica	49.72 " "
Lime	0.86 " "
Magnesia	0.73 " "
Potash	0.42 " "
Soda	4.68 " "
Sulfuric anhydrid	1.46 " "
Boracic acid (by difference)	6.34 " "
	100.00

The chemical formula of the glaze, then, is—

$$\left.\begin{matrix} 0.4952\ PbO \\ 0.1296\ CaO \\ 0.3752\ Na_2O \end{matrix}\right\} 0.5728\ Al_2O_3 \left\{\begin{matrix} 3.780\ SiO_2 \\ 0.413\ BO_3 \end{matrix}\right.$$

1.0 RO

In order to make this glaze, one would melt together to form a fritt—

			Parts	give	Melted.
0.207	equivalent	borax.....	39.5	borax glass	20.91
0.168	"	soda ash ...	8.9	Na_2O	5.21
0.130	"	whiting....	6.5	CaO	3.64
0.100	"	china clay .	13.0	$Al_2O_3 2SiO_2$	11.15
0.800	"	flint.	24.0	SiO_2	24.00
			The charge 91.9	melts to...	64.91

For the glaze, grind together—

0.4952	equivalent	white lead.....	64.23
0.4128	"	china clay.....	53.46
2.78	equivalents	flint.....	83.4
		fritt.....	64.91
			266.00

It will be noted that the analysis contains an appreciable amount of sulfuric anhydrid, which was ignored in the calculation of the analysis.

The analytical sample was taken from the edges of the tile, where the glaze was thickest; but here, although not over the surface of the glaze generally, there was a crystalline scum. This was "glass-gall," or a crystalline separation of sulfates. The proportion of sulfuric anhydrid was therefore larger than if the sample had been averaged over the entire face.

Sulfates are highly objectionable in glazes. They may form either unsightly crystalline separations on the edges of the ware, or cover its entire face with a very thin greasy scum, and when present in large amounts, may float in drops on the glaze, from which, on cooling, they may easily be pinched out, leaving pits in its surface.

The chemist must make certain that the materials are

free from sulfates, and even look, at times, to the water in which the glazes are ground.

Sulfates are frequently formed by the absorption of sulfuric anhydrid generated in the kiln from the burning of a very sulfurous coal. Obviating difficulties that may arise from this will be discussed under the subject of firing. It may merely be noted here that the phenomenon, commonly called "sulfuring" by potters, is the reduction of the lead of the glaze, and is often the catchword with which a careless fireman tries to throw on the fuel, the responsibility for inattention to clinkering or other manipulations affecting the draught in firing.

The phenomenon of a reduction of the glaze frequently hangs together, in so far, with the presence of a large amount of sulfur, in that the coal contains the latter, mainly in the form of iron pyrites, which, leaving on burning the iron oxids, give a more or less fusible ash, or clinker, which is very liable to choke off a part of the necessary air supply.

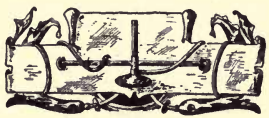
The range of formulas of pottery and porcelain glazes is from—

$$1\ RO\ 0.1\ R_2O_3\ 1.5\ SiO_2$$
$$\text{to}\ \ 1\ RO\ 1.2\ R_2O_3\ 12\ SiO_2,$$

and the corresponding range of temperatures required in their burning is from the melting point of silver, or pyrometric cone 010 of Cramer's scale, to pyrometric cone 18 of Seger's scale, probably equivalent to the melting point of an alloy—eighty per cent. platinum, and twenty per cent. gold.

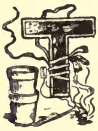
In this wide range of possible compounds, the one suit-

ing the particular conditions demanded by the clay used, and the process of manufacture, and the uses to which the ware is to be put, must be sought. For the potter to do this empirically is certainly a very difficult and uncertain undertaking; for the chemist, beginning with a mixture based on a definite chemical formula within the given limits, and systematically introducing the various possible elements in proportions varying by definite equivalents, it is but a question of time to get the desired formula, which, with experience and skill in experimenting, need not take long.



CHAPTER VI.

RED WARE.



THE simplest and cheapest of glazed pottery is called from its color, "red ware." It is ordinarily formed from the same materials used for making red brick; alluvial mud found in the river valleys and weathered ferruginous shales. It is important that the material contain but little lime, which if present in any considerable amount, destroys the bright red color imparted by the iron oxid, giving unsightly ware.

At a heat sufficient to melt a wire of pure silver to a bead, the clay should bake so hard that it can barely be cut with a knife. The specimen baked at that heat should adhere when touched to the tongue, and be of a bright red color.

The clay must be of such composition that with the hardness attained at the given temperature (from the melting point of silver to not exceeding that of an alloy of seventy-five per cent. silver, twenty-five per cent. gold), it will have practically the same coefficient of expansion, and hence bear without fracture, a glass fusible at that heat.

A glass or "glaze" of this character would be one having a chemical formula lying between $1PbO$, $0.1Al_2O_3$, $1SiO_2$ and $1PbO$, $0.15Al_2O_3$, $1.5SiO_2$ made by

grinding together 129.7 parts white lead, 13.0 to 19.5 parts china clay, and 24 to 21 parts quartz.

In order to absolutely resist the action of acids on cooking utensils of "red ware," it would be desirable to use more acid glazes, but such is not the practice in this industry; although there is a practice that should be absolutely condemned and against which chemists should throw their influence, namely, that of using litharge or galena alone as the glazing substance and depending on its taking up sufficient alumina and silica from the body of the ware, during fire, to form the glass. A glaze so formed is certain to be basic on the surface, and is sure to be attacked by the weakest acids used in cookery.

The red ware potter has no china clay at his disposal, and usually makes his glaze by grinding the lead preparation with a loamy sand.

The glaze then has frequently some such composition as this—

$$1PbO \left\{ \begin{matrix} 0.09Al_2O_3 \\ 0.03Fe_2O_3 \end{matrix} \right. 1.4SiO_2$$

(taken from practice). This glaze would be of a yellowish color, which is not objectionable.

The coefficient of expansion of the clay depends on the amount and fineness of the uncombined silica and feldspathic detritus it contains, which constituents are determined by the "rational analysis."

A practical "red ware" clay, burning at the indicated temperature to the required hardness and color, and bearing the glaze without suffering fracture ("shivering") or the glaze itself cracking ("crazing"), being of suffi-

cient plasticity and having from the clay to the baked condition a linear shrinkage of six per cent., is a weathered shale of the following analysis:

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4 and Na_2CO_3.
Silica	74.75	57.20
Alumina	12.55	0.62
Ferric oxid	5.28	0.70
Lime	1.28	0.77
Magnesia	0.85	0.00
Alkalies	2.27	1.80
Combined water	3.23	
	100.21	61.09

RATIONAL ANALYSIS.

	Per cent.
Clay substance	39.12
Quartz	52.54
Feldspathic detritus	8.55

PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	44.86
Alumina	30.50
Ferric oxid	11.71
Lime	1.30
Magnesia	2.17
Alkalies	1.20
Combined water	8.26
	100.00

The following, a highly plastic red colored clay, proved unsuitable. It was too plastic and would twist and crack in the fire; it burned to a dark brownish red, instead of a light bright color, shrinking twelve per cent. in the fire. It contains insufficient uncombined silica to

bear a glaze suited to the red ware fire, without the latter's "crazing."

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4 and Na_2CO_3.
Silica	61.93	28.98
Alumina	19.87	0.53
Ferric oxid	7.83	1.57
Lime	1.61	0.16
Magnesia	0.77	0.08
Alkalies	2.38	1.08
Combined water	5.91	
	100.30	32.40

RATIONAL ANALYSIS.

	Per cent.
Clay substance	67.90
Quartz	21.57
Feldspathic detritus	10.83

PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	48.53
Alumina	28.48
Ferric oxid	9.22
Lime	2.14
Magnesia	1.02
Alkalies	1.92
Combined water	8.70

PRODUCTS.—The wares manufactured in this industry are flower-pots and other unglazed terra-cotta articles; of glazed articles, brown door-knobs, milk crocks, bean pots, and other cooking vessels, pots for corroding white lead, jardiniers, umbrella-stands, spittoons, etc., which latter ornamental pieces are often decorated on the outer unglazed surface with oil colors.

With the exception of these crudely ornamented products, the common occurrence of the raw material of this industry has led potters to abandon it to the meanest uses, although the decorative possibilities of red-ware are great.

This may be seen in the Pennsylvania Dutch pottery of the last century and in the red faience of the Rookwood pottery of to-day.

The former ware,[1] fashioned of red clay, was dipped in a "slip" of white-burning clay, and through the thin white coat thus deposited on the body of the pieces, designs were etched with a sharp point, appearing as dark red lines in a white field, resembling the *sgraffito* mural decoration of Italy.

The ware was often painted with mineral colors; before burning it was covered with a mixture producing a clear glaze in the fire.

The red Rookwood faience is made of a highly ferruginous shale, from the Ohio river, mixed with some kaolin, making it more resisting to the fire and giving the baked clay a lighter and more brilliant red color. It differs from ordinary red ware, in process of manufacture, in that the clays are mixed and washed and the pieces finished in two fires, as in the case of yellow ware, to be described in the next chapter.

The decoration consists in clouded grounds of underglaze colors, applied with the air-brush and hand-painted designs, done in "slips" stained with the same hard-fire colors.

[1] E. A. Barber, The Pottery and Porcelain of the United States, p. 66, 1893.

All decoration is applied to the freshly formed ware, when in a leather-hard condition, and the dried pieces are baked at a temperature of about the melting down of pyrometric cone seven.

Drawn from this kiln, the ware is, without further treatment, dipped in a ferruginous glaze, having the chemical formula:

$$\left.\begin{matrix} 0.77PbO \\ 0.15K_2O \\ 0.08CaO \end{matrix}\right\} \left.\begin{matrix} 0.15Al_2O_3 \\ 0.07Fe_2O_3 \end{matrix}\right\} 1.59SiO_2$$

The second or "glost" fire to which it is then subjected being about of the temperature necessary to melt silver.

When the ground color consists of chrome oxid or iron chromate or colors containing these, a prolonged or repeated glost fire may convert the above glaze over them into an aventurine glass. Being nearly saturated with iron it will, under favorable conditions over chrome-colors, become supersaturated with iron chromate, which, under suitable conditions of cooling, separates from the glaze in crystalline spangles, which have a brilliant golden reflection.

When the faces of the crystals are turned in all directions the glaze often resembles aventurine quartz; when the glaze still flowed or dragged down on the piece during the crystallization, the crystals are often ranged in rows with the faces turned in one direction, giving a reflection, as do the filaments of asbestos in cat's-eye chalcedony.

Similar crystallizations can be produced in other glazes and on other bodies, but only on the red or on a darker ground and through the medium of an amber-yellow glass, is the effect striking and beautiful.

EXAMINATION OF MATERIALS.—If the rational analysis of a clay and its general appearance indicate that it may be serviceable for making red-ware, tests should be made to determine its plasticity and its binding property.

It is also important to wash a larger dried sample through a set of graded sieves and record the percentages of sand and other coarser impurities remaining on each, in order that the potter may know whether these are present in amounts and of a character that would present mechanical objections in fashioning and burning the ware.

Cakes several inches square and about $\frac{3}{16}$ inch thick, should be formed and dried and placed in a muffle with a wire of pure silver; on one or two of the cakes such a a glaze-mixture as described before should be painted to the depth of about $\frac{1}{32}$ inch. The muffle is then fired with a gradually increasing heat until in the course of three hours, the silver wire melts, when firing is discontinued.

It goes without saying that an oxidizing fire must be maintained throughout the burning, in order to insure a bright red color of the clay by complete oxidation of its iron and to prevent a reduction of the lead of the glaze.

When cold the pieces are withdrawn and the color and hardness of the unglazed ("biscuit") pieces and the character of the glazed sherds, and whether, in the course of

some weeks the latter bear the glaze without defect, are noted.

"Slips" for ornamenting wares, as described, are made by softening white plastic clays or mixtures resembling the white-ware bodies to be described later in water and passing the creamy mixture through a fine sieve.

For engobing ware, as in the case of the Pennsylvania Dutch potteries, this "slip" is left liquid enough to allow the pieces to be immersed in it, and remain, after their withdrawal, covered with a smooth, entirely opaque deposit.

For painting, the slip is thickened to the consistence of common tube-paints and colored with metallic oxides.

In either case the question for the chemist is the selection of a white clay or mixture that does not crack or shell off from the particular clay upon which it is to be applied, during the processes of drying and firing.

This selection can only be made by empiric trials, as differences in shrinkage both during the first step of drying and the second of burning between the body and the slip applied to it, differences too subtle for direct measurement, would be fatal to the result.

The trials need only be made, however, with the one object of uniformity in shrinkage between the body and the slip. The latter has no influence on the crazing or shivering of the glaze, which is applied over it, provided that the body is suited in its coefficient of expansion to the glaze.

CHAPTER VII.

ROCKINGHAM AND YELLOW WARE.

HIGHER grade of ware, than that last treated is "Rockingham and Yellow Ware;" though belonging to the same ceramic category, namely, "Faience," in that it also consists of a porous body covered with a transparent lead glaze.

It differs from "red ware" in color, and in having a body requiring a higher temperature for its proper burning, so that the glaze is not applied to the freshly formed pieces in their "clay state," but to the once baked or "biscuit" pieces, and is then finished in a second or "glost" fire softer than the first.

The clays used for "yellow ware" belong to the class commercially known as second-class fire clays; the same from which common firebrick and such terra-cotta articles as stove and flue-linings, chimney-tops, garden vases, etc., are made. They are generally the common "buff" or "blue" clays of the coal measures and are widely distributed in all our carboniferous exposures.

A typical clay of this character has the following composition:

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4 Per cent.
Silica	60.50	22.33
Alumina	25.53	0.53

	Per cent.	Insol. in H_2SO_4. Per cent.
Ferric oxid	1.66	0.26
Titanic oxid	0.54	....
Manganous oxid	0.33	....
Lime	0.38	0.26
Magnesia	1.19	0.07
Alkalies	1.76	0.37
Combined water	7.98	....
	99.87	23.82

RATIONAL ANALYSIS.

	Per cent.
Clay substance	76.05
Quartz	19.54
Feldspathic detritus	4.28
	99.87

CHEMICAL COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	50.19
Alumina	32.87
Ferric oxid	1.84
Titanic oxid	0.71
Manganous oxid	0.43
Lime	0.16
Magnesia	1.47
Alkalies	1.82
Combined water	10.50

The yellow-ware potter is better equipped in machinery than the red-ware potter, and does not, like the latter, prepare his clay by merely soaking it with water and then tread and knead it to a plastic mass of the proper consistence; but subjects the clay to a regular washing process. Hence the presence of a certain amount of coarse sand,

and nodules and particles of iron pyrites, very commonly found in all such clays, do not spoil them for his work, as they are removed by the necessary and customary process of manufacture.

This consists in "slipping" the clay in a vat with mechanical stirrers, known as a "blunger," sifting the "slip" through a sixty-mesh wire sieve or a No. 8 silk lawn stretched over a vibrating frame, from which the coarser sandy impurities are thrown, and condensing the "slip" to plastic clay by evaporation or by a filter-press.

From this process, it will be realized that the original clay must be in such a condition of physical aggregation as to be easily disintegrated or "slipped" by mere stirring in water. A hard clay, readily reduced by the elements in "weathering" to such a condition, will also answer the purpose; but the double shoveling involved in transferring clay from the bank to a weathering flat, and from thence, after six months or a year's exposure to the elements, to the factory, is a trouble the potter avoids if he can.*

There is a class of clays, which from their composition are admirably adapted for yellow ware, but have remained completely barred from this use because of their physical character. These are the "flint clays" of which the following analysis is typical:

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4. Per cent.
Silica	55.04	16.96
Alumina	29.85	0.11
Ferric oxid	1.76	....

	Per cent.	Insol. in H_2SO_4. Per cent.
Lime	0.79	0.12
Magnesia	0.57	0.17
Alkalies	1.83	0.58
Combined water	10.95	....
	100.79	17.94

RATIONAL ANALYSIS.

	Per cent.
Clay substance	82.85
Quartz	16.58
Feldspathic detritus	1.35
	100.78

PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	45.97
Alumina	35.90
Ferric oxid	2.12
Lime	0.81
Magnesia	0.48
Alkalies	1.51
Combined water	13.22
	100.00

This clay occurs in rocky masses having a conchoidal fracture, the splinters of which are so hard and sharp, that a flying piece, struck off with the pick, will cut the hand or face. It eagerly absorbs water and with a crackling noise, though without noticeable evolution of heat, falls to pieces, yielding a mass of shell-like splinters, though a year's exposure to the weather, while reducing it to a fine sand, fails to produce a workable clay. Simple grinding in water and thickening the resulting "slip,"

by any convenient method, produces a highly plastic mass, that is readily formed into ware, burns to a bright yellow color, and bears the customary yellow ware glazes with less danger of "crazing" than the before-mentioned and commonly used clay. This latter fact is to be accounted for by the extreme fineness of the contained quartz, more than compensating for the reduced quantity of the same.

The expense of wet-grinding a "flint clay "would not be excessive, but the introduction of machinery for the purpose, in so conservative a craft as the one under consideration, would be met with almost stolid resistance.

The first or "biscuit" fire of yellow ware, for hardening the clay pieces, must reach "good biscuit heat," that is a temperature sufficient to bake the clay so hard that it can no longer be cut with a knife, but that the steel leaves a lead-pencil-like mark on the surface. At the same time, the sherd must still be porous and adhere when touched to the tongue.

The temperature of the "biscuit" fire will necessarily, of course, vary with the chemical and physical character of the clay used. The potter determines it empirically by testing-trials of the clay drawn from the kiln, with his knife and tongue.

It is very important that the chemist determine at what heat the clay he is examining attain a "good biscuit" condition, in order that the potter may know whether he can introduce ware made of it into his biscuit kiln along with his old ware. As a kiln of ware represents considerable capital exposed to a risky operation, potters nat-

urally are absolutely opposed to the adoption of new clays requiring different conditions of fire from those already adopted by them; these must dovetail easily at least into their kiln conditions, by requiring the same heat.

Yellow-ware clays reach the required hardness at temperatures varying from the melting points of pyrometric cones five to seven or even eight.

For "yellow ware" as for "red ware," it is customary to employ a "raw" glaze, that is, one containing no soluble constituents which have first to be rendered insoluble by fritting to a glass.

The customary type of glaze has a formula resembling one of the following: 1 PbO, 0.2 Al_2O_3, 2 SiO_2, which may be made by grinding together 129.7 white lead, 25.9 china clay, and 48 flint.

$$\left.\begin{matrix} 0.8PbO \\ 0.2K_2O \end{matrix}\right\} 0.2Al_2O_3, 2SiO_2 \text{ from}$$

$$1.0$$

103.8 white lead, 55.7 feldspar, and 24 quartz.

$$\left.\begin{matrix} 0.8PbO \\ 0.1CaO \\ 0.1K_2O \end{matrix}\right\} 0.2Al_2O_3, 2SiO_2.$$

$$1.0$$

obtained by grinding together 103.8 white lead, 27.9 feldspar, 13 china clay, 5 calcium carbonate, and 36 quartz.

The acidity of the glaze generally varies from one and

eight-tenths to two and two-tenths SiO_2, depending upon the amount of quartz contained in the clay upon which it is expected to stand. The alumina will similarly vary from 0.16 to 0.2 and over according to the stiffness of the glaze required and the conditions of firing, causing a liability to devitrification, or most likely as chance has thrown a fairly satisfactory formula into the potter's hands.

The temperature at which the glazes run bright lies about at a point at which an alloy composed of fifty per cent. silver and fifty per cent. gold will melt, though depending upon the composition of the glaze, and the length of fire, the melting point of the alloy, seventy-five per cent. gold and twenty-five per cent. silver may have to be reached.

"Rockingham ware" differs from "yellow ware" only in that it is covered with a brown manganiferous glaze, applied either by spattering the piece, previously dipped in the clear glaze, with the same, thus producing a mottled effect by the melting of the glazes into each other, or by directly dipping the biscuit piece into the "Rockingham" glaze alone, whereby the fired piece obtains a uniform red-brown finish.

Common forms of Rockingham glazes are the following:

$$\left.\begin{matrix} 0.85PbO \\ 0.15MnO \end{matrix}\right\} 0.18Al_2O_3,\ 1.8SiO_2$$

$$1.00$$

made by grinding together 110 white lead, 6.5 manganese dioxid, 23.3 china clay, and 43.2 flint;

also,

$$\left.\begin{matrix} 0.9PbO \\ 0.1MnO \end{matrix}\right\} \left\{ 0.15Al_2O_3 \right\} 2SiO_2$$
$$\left\{ 0.05Fe_2O_3 \right\}$$

1.0

similarly prepared with a ferruginous clay, the formula of which any chemist will be able to figure out from the equivalent proportions given.

As in the case of "red ware" the prevailing fire of both the biscuit and glost kilns should be oxidizing.

PRODUCTS.—The ware manufactured in this industry embraces such kitchen and other domestic utensils as bowls, bakers, nappies, chambers, tea and coffee-pots, pitchers, etc.

Classes of ornamental pottery closely allied to yellow-ware and readily developed in connection with it, inasmuch as they require similar raw materials and conditions of firing, are those known as "Limoges" and "Barbotine."

In both of these, the freshly formed ware is decorated by painting with "slips" of white plastic clay, mixed with under-glaze colors. In Barbotine ware, this decoration is supplemented with ornaments and flowers modeled in high relief directly on the pieces.

Thus finished, the ware is dried and burned in biscuit, after which treatment, it is covered with a clear yellow-ware glaze and burned in the glost-kiln.

EXAMINATION OF THE MATERIALS.—In examining a clay for its possible use in this manufacture it is important to determine whether it can readily be disinte-

grated by stirring or boiling in water, or whether repeated soaking and drying or freezing and thawing bring it to such a state.

A "slip" of the clay should be run through a sixty mesh wire sieve and the amount and character of the remaining sand given.

If the latter is at all appreciable the sample for analysis should not be taken from the crude clay, as this would, of course, give an entirely false idea of the constituents ultimately entering the potter's "body," but the sample should be taken from the thickened and dried "slip" which has passed the sixty mesh sieve. Such a "slip" is readily thickened by pouring it on a thick, clean, and dry slab of plaster of Paris, which readily absorbs the water and from which the plastic clay is easily peeled without danger of contamination with plaster.

A part of the now plastic clay is dried for preparation of the sample for a rational analysis, in the customary manner. The bulk of the washed product is formed into cakes and rings for the burning. The latter are made for the purpose of watching the progress made by the clay in the fire, and determining when the baking is finished. These rings should be of such size, as to be readily withdrawn from the muffle with a stout iron wire, through the spy-hole in the door of the same.

When the clay pieces are bone-dry, they are placed in the muffle on a thick bed of clean quartz sand or a thick fire-clay tile strewn with the same.

The rings should be so placed as to be easily reached through the spy-hole in the door brick and parallel with

them the Seger cones five, six, seven and eight, should be set upright on a piece of tiling or flat cake of baked or raw clay, to which they had best be stuck with a little "slip." The door brick is then luted in place with a wad of soft clay, and the firing begun gradually, raising the heat at an increasing rate.

Should there be difficulty in seeing the pyroscopes when the muffle has reached bright redness, on removing the plug from the spy-hole, the careful introduction of a thick iron wire in their neighborhood, will momentarily so far reduce their temperature as to make them clearly discernible against the bright walls of the muffle.

When cone five crooks over, the first clay ring should be drawn from the muffle with a wire and when cool, tested with the knife for hardness; if insufficient the firing is continued until cone five has melted down completely, when the second ring is drawn. The next trial is drawn at the crooking of cone six, and so on until a heat is reached at which the clay trial ring is sufficiently hard to resist cutting with a knife, without having lost all porosity, adhering when touched to the tongue.

When this heat is reached the firing is discontinued and the furnace allowed to cool.

The fired pieces of clay removed from the cold muffle are covered on one side with one of the described glazes, of which the first is recommended, being easily made and fired as a convenient empirical standard, against which to test the coefficient of expansion of the baked clay.

The pieces are then baked a second time to melt the

glaze upon them, the heat reached being that of the melting-point of the alloy, fifty per cent. silver and fifty per cent. gold.

It is also very convenient to use the small baked trial rings partly covered with the glaze as trials for this fire, the firing being discontinued when the glaze on one of these rings drawn from the muffle has run bright.

The color of the clay under the clear glaze should be described. Tints approaching bright straw and lemon-yellows are the ones sought after. Brownish and reddish tints are not acceptable to the trade buying the ware.

The behavior of the glaze on the clay must also be given. From these data the potter will be able to determine whether the acidity of his glaze must be increased or diminished, or which clays to mix, if he choose to keep the glaze as it is and compensate the incorrect coefficient of expansion of the clays by mixing them.

Slips for underglaze painting in the Limoges manner must be found empirically for the particular yellow-ware body upon which they are to be used.

The clays for executing the high-relief Barbotine modeling must bear the glaze that is finally to be applied to the ware without fault. They are usually mixed after the manner of white-ware bodies, to be described in a subsequent chapter. A number of such mixtures must be found that will bear the yellow-ware glaze, and among these such a one is selected that will in its shrinkages conform with those of the yellow body upon which it is to be applied.

CHAPTER VIII.

STONEWARE.

THE products belonging to Brogniart's second class, sixth division, are perhaps next to common building brick, the most important of ceramic manufactures.

Such articles as milk and butter crocks, jars for acid liquids, sewer-piping, and vitreous paving brick being needed in large quantities and the purposes to which they are put, precluding other than the very cheapest wares, the sole aim of American manufacturers has turned in the direction of improvement in the mechanical engineering of their plants and not in that of materially improving the ware itself.

But even in the engineering of such factories there is still great room for progress. Thus it is unlikely that there is as yet a single continuous kiln in operation in one of the branches of this industry in the country, although the relative cost of fuel to product is such that the heat wasted in intermittent kilns represents an appreciable percentage of cost.

And further, as the ware is piled up openly in the kiln, without the protection of saggars and is frequently damaged by the ferruginous ash, carried into the kilns from the firings by the strong draught, the fuel should

be converted into gas in producers, before being admitted to the kilns. This can only be rationally done in conjunction with continuous firing.

Besides cheapening the production, chemists must be particularly interested in improving the quality of stoneware, as it is the material in which, on a manufacturing scale, all those operations are performed which in the laboratory require the use of porcelain, glass, and platinum.

Our chemical industries cannot attain great proportions until stoneware condensing jars and worms, tanks, siphons, plate-towers, acid-pumps, pyrites roasting plates, are as plentifully and cheaply manufactured here and of as good quality as abroad.

As wrought iron has artistic qualities that in its way cannot be equaled by more costly metals, so stoneware has decorative possibilities far beyond those of the various white wares, in faience or even porcelain, upon which too much ingenuity has been spent. The old German and Flemish stonewares amply prove this, as do also, in their several ways, the modern productions of Doulton in Lambeth, Villeroy and Boch in Mettlach and Merzig and the Banko-ware of Japan.

In the main, the same class of clays as those used in the yellow-ware industry, are employed for making stoneware. The difference in the body of the two products being the result of the difference in temperature to which they are subjected.

The body of yellow ware is burned until it can no longer be scratched with a steel point, but it must still

be sufficiently porous to adhere strongly when touched to the tongue, and it must not have lost its bright yellow color. Stoneware is burned until the clay has become vitreous and is of a greyish stone color.

Clay suitable for stoneware must be free from stony concretions and larger particles of iron pyrites, as it is not customary, in this work, to purify the clay as the yellow-ware potter does.

In the country shops the potter merely soaks and tramps his clay to homogeneity; in the factories the same is accomplished by grinding the wet clay under runners in the horizontal "wet-pan."

In many of the newer factories, it is true, the clay which is to be formed in plaster molds is subjected to a washing process, as in the preparation of the material of the industry last described. But those who form their ware free-hand on the potter's wheel insist that a clay loses much of its plasticity in washing, becoming "punky," that is, elastic rather than plastic. Whether this is merely a conservative prejudice or has an element of truth in it, has not, as yet, been proven.

The requirement remains that a clay for stoneware must be pure enough not to need washing.

The first clay of which the analysis is given, in the preceding chapter, is suitable for stoneware and is used for the purpose. However, a clay a little richer in alkali and rather more siliceous would be better, especially if the ware is to be salt-glazed, as it would then come of a more uniform stone-grey color and take the salt-glazing more perfectly.

The following analysis is of the clay used in one of the larger factories, making a ware of typical character:

	The entire clay contains	Portion insoluble in H_2SO_4 contains
	Per cent.	Per cent.
Silica	71.58	46.06
Alumina	18.31	0.43
Ferric oxid	1.09	0.04
Lime	0.40	0.23
Magnesia	0.62	0.10
Alkalies[1]	2.96	0.63
Combined water	5.95	0.00
Manganous oxid	trace	0.00
	100.91	47.49

RATIONAL ANALYSIS.

	Per cent.
Clay substance	53.42
Quartz	44.41
Feldspathic detritus	3.08
	100.91

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	47.70
Alumina	33.47
Ferric oxid	1.96
Lime	0.31
Magnesia	0.97
Alkalies	4.36
Combined water	11.13
	99.90

The alkali in the above clay is about as high as it dare be under ordinary circumstances, for as stoneware is

[1] Combining weight of the alkalies 47.00 per cent.

burned to vitreousness, there is danger of the pieces collapsing in the fire, if the clay be too fusible.

Like all vitreous ware, stoneware, unless it be quite thin and very evenly formed as are porcelain crucibles, dishes, and beakers for laboratory use, is sensitive to sudden heating and cooling.

Cooking-crocks and such other vessels, which are to be subjected to these conditions, are made to come hard, but still quite porous in the stoneware fire. They are not stoneware, properly speaking, though generally manufactured with it.

The clays used for making such products contain a large percentage of sharp quartz sand. Where they do not occur, they may be made by mixing quartz sand with a clay that is, in the main, more aluminous and less rich in alkali than a stoneware clay.

Stoneware is fired but once, its glaze being applied before or during that operation, and melted while the clay is hardening to the proper character. It is either salt- or slip-glazed—that is, it has either a very thin blush of a soda-glass on its surface, produced by volatilizing common salt in the kiln, when the fire has reached its highest point, or before placing in the kiln, it is coated with a fusible ferruginous clay which melts at the heat in which the body of the ware is properly baked. Most stoneware is salt-glazed on the outside and slip-glazed on the inside where the salt-vapor can not reach, owing to the fact that the pieces set on top of one another in the kiln mutually protect their inner surfaces from the kiln atmosphere.

The stoneware potter fires his kilns altogether by "slip-trials;" these are pieces of his clay dipped in the "slip" or glazing-clay and suitably placed in the kiln opposite the trial holes, where they can be reached with an iron hook and withdrawn one by one for inspection as the fire progresses. When the slip-clay has thoroughly melted and attained a bright brownish-black color, the proper heat is considered to be reached.

If the ware is to be salt-glazed, a certain amount of salt is then thrown at regular intervals into the kiln-mouths, together with green wood, which gives the water vapor necessary to decompose the fumes of sodium chlorid and set the alkali free for combination with the alumina and silica on the surface of the body of the ware.

If the ware is entirely slip-glazed, the firing, on reaching the proper temperature, is merely discontinued.

In almost all of the stoneware potteries of the United States, the temperature reached is that of the melting of Seger's pyrometric cone eight.

The reason of the rather surprising uniformity of the heat adopted in practically all of the establishments making this ware, and irrespective of the clays they are using for the body of the product, lies in the fact that this is the heat required to melt one particular slip-clay. This, on account of its convenience in several of its physical properties, particularly on account of its great uniformity in color and melting-point, is used in nearly all of the stoneware potteries of the country for glazing their ware. Even where other slip-clays are used for this purpose, the temperature of the kilns was at least originally

adopted for the use of this slip, and it is used for the firing trials, if not for glazing the ware itself.

An analysis of this clay, which is mined near Albany, New York, and is commonly known as "Albany slip," runs as follows:

	The entire clay contains	The portion insoluble in H_2SO_4 contains
	Per cent.	Per cent.
Silica	58.54	38.36
Alumina	15.41	2.33
Ferric oxid	3.19	0.12
Lime	6.30	1.42
Magnesia	3.40	0.15
Alkalies[1]	4.45	2.65
Carbon dioxid	6.85	....
Sulfur trioxid	1.10	....
Phosphorus pentoxid	trace	....
Combined water	1.23	....
	100.47	45.03

RATIONAL ANALYSIS.

	Per cent.
Clay substance	39.35
Feldspathic detritus	15.31
Quartz	29.72
Calcium sulfate	1.87
Calcium carbonate	7.09
Magnesium carbonate	7.13
	100.47

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	51.09
Alumina	33.12

[1] Combining weight 45.8.

	Per cent.
Ferric oxid	7.70
Lime	0.35
Alkalies	4.55
Combined water	3.11
	99.92

As this clay is used upon the ware as a glaze, it is important to calculate from its gross analysis the chemical formula that the glass resulting from melting it will have, in order to find the type of glaze required in this industry; to be able to reproduce it from other materials; or to systematically modify it for the purpose of producing glazes of lower or higher melting-points, to accommodate clays that should be burned at temperatures other than those required for this particular slip-glaze.

The chemical formula of the Albany slip-glaze, calculated from the above analysis, would be:

$$\left.\begin{matrix} 0.1954\ K_2O \\ 0.4592\ CaO \\ 0.3454\ MgO \end{matrix}\right\} \left.\begin{matrix} 0.6080\ Al_2O_3 \\ 0.0810\ Fe_2O_3 \end{matrix}\right\} 3.965\ SiO_2.$$

$$1.0\ RO \qquad 0.689\ R_2O_3$$

The following slip-glaze, which is also burned at about the same heat with the Albany, becomes of a rich red-brown color; it is composed of a mixture of fusible clays, the proportions having been established empirically, are kept secret and are unknown to the writer.

	Per cent.
Silica	55.67
Alumina	14.18
Ferric oxid	3.56
Lime	8.00
Magnesia	2.84

	Per cent.
Manganous oxid	0.41
Alkalies[1]	5.01
Sulfur trioxid	1.11
Combined water and carbon dioxid	9.87
	100.65

The chemical formula of the glaze resulting from melting the above would be:

$$\left.\begin{matrix} 0.2290\ KNaO \\ 0.0203\ MnO \\ 0.2492\ MgO \\ 0.5015\ CaO \end{matrix}\right\} \left.\begin{matrix} 0.4832\ Al_2O_3 \\ 0.0781\ Fe_2O_3 \end{matrix}\right\} 3.258\ SiO_2.$$

$$1.0\ RO \qquad 0.5613\ R_2O_3$$

It appears from these formulas that the common slip-glaze for stoneware must have a chemical formula not differing widely from that of Seger's pyrometric cone number two, namely:

$$\left.\begin{matrix} 0.25\ K_2O \\ 0.75\ CaO \end{matrix}\right\} \left.\begin{matrix} 0.4\ Al_2O_3 \\ 0.1\ Fe_2O_3 \end{matrix}\right\} 4SiO_2.$$

$$1.0\ RO \qquad 0.5\ R_2O_3$$

As clays high in mineral detritus are common, abounding especially along the borders of former glaciation, the chemist may frequently be called upon to show the stoneware potter how a local slip-clay should be mixed in order to melt in a fire most suitable for the body of his ware.

It is commonly believed by potters, and also by chemists, that if a clay be infusible, it is only necessary to add sufficiently of some basic material, as an alkali, alkaline

[1] Combining weight 38.4.

earth, litharge or ferric oxid to obtain a glass. This is not the case, as the relation of the R_2O_3 elements to silica is vital and a glaze of this type may be infusible from being too basic. The chemist on working out the chemical formula of the clay, which it is desired to use, will frequently find it to be too aluminous, requiring the addition of silica quite as much as that of a base.

In order to illustrate this, systematic experiments were made with a slip-clay that merely softened and swelled up at the melting down of pyrometric cone eight, but was far too infusible to run at that heat. It analyzed as follows:

	The entire clay contains	The portion insoluble in H_2SO_4 and Na_2CO_3 contains
	Per cent.	Per cent.
Silica	56.59	23.56
Alumina	25.96	1.00
Ferric oxid	2.30	0.07
Lime	1.60	0.06
Magnesia	1.90	0.10
Alkalies[1]	5.33	0.40
Combined water	6.22	....
Sulfuric anhydrid	1.07	....
	100.97	25.19

RATIONAL ANALYSIS.

	Per cent.
Clay substance	73.96
Feldspathic detritus	5.44
Quartz	19.75
Calcium sulfate	1.82
	100.97

[1] Combining weight 31.

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	44.65
Alumina	33.74
Ferric oxid	3.01
Lime	1.09
Magnesia	2.43
Soda	6.66
Combined water	8.40

CHEMICAL FORMULA OF THE MELTED CLAY.

$$\left.\begin{matrix} 0.5305\ Na_2O \\ 0.1763\ CaO \\ 0.2932\ MgO \end{matrix}\right\} \left.\begin{matrix} 1.5550\ Al_2O_3 \\ 0.0887\ Fe_2O_3 \end{matrix}\right\} 5.82\ SiO_2$$

$$1.0\ RO \qquad 1.6437\ R_2O_3$$

Combining weight of the clay according to this formula, 308.5.

In order to make a slip-glaze with this clay the following trial mixtures were ground with water in a mortar and poured over cakes of stoneware clay, in a leather-hard condition, forming a deposit on each one millimeter thick. The pieces were subjected, after drying, to the heat of the stoneware kiln.

A.
$$\left.\begin{matrix} 0.1768\ Na_2O \\ 0.0977\ MgO \\ 0.7255\ CaO \end{matrix}\right\} \left.\begin{matrix} 0.518\ Al_2O_3 \\ 0.1\ \ Fe_2O_3 \end{matrix}\right\} 4SiO_2.$$

$$1.0\ RO \qquad 0.618R_2O_3$$

made by grinding together

102.8	parts	of the	slip clay.
33.3	"	"	whiting.
61.8	"	"	flint.
5.6	"	"	ferric oxid.

B.

$$\left.\begin{matrix} 0.2826\ KNaO \\ 0.6441\ CaO \\ 0.0733\ MgO \end{matrix}\right\} \left.\begin{matrix} 0.5387\ Al_2O_3 \\ 0.1022\ Fe_2O_3 \end{matrix}\right\} 3SiO_2.$$

$$1.0\ RO \qquad 0.6409\ R_2O_3$$

made of

77.1 parts of the slip clay.
41.5 " " feldspar.
30.0 " " whiting.
19.0 " " flint.
6.4 " " ferric oxid.

C. Like B, but with increased silica.

$$1.0\ RO\ \ 0.6409\ R_2O_3\ \ 4SiO_2.$$

taking for the mixture

77.1 parts of the slip clay.
41.5 " " feldspar.
30.0 " " whiting.
49.0 " " flint.
6.4 " " ferric oxid.

D. With a further increase of silica containing

77.1 parts of the slip clay.
41.5 " " feldspar.
30.0 " " whiting.
79.0 " " flint.
6.4 " " ferric oxid.

A, containing insufficient alkali, melted to a puckered greenish-brown coat, with little in its appearance to characterize it as a glass. The increased alkali in the following trials overcame this defect, they being bright and glass-like.

B, while presenting the appearance of a dark-brown glass, was devitrified at the edges and contained throughout whitish crystalline separations resembling the "figging" of certain transparent soaps.

D was insufficiently fused, but appeared otherwise as a perfect glass.

C presented a brownish-black, highly lustrous glass, having in every particular the character of a perfect stoneware slip-glaze.

These experiments show that any fusible clay can be mixed to make a "slip-glaze." The use of a particular clay for the purpose is only profitable, however, when it is quite low in alumina and very high in alkalies.

Alkaline earths, ferric oxid, and silica are easily and cheaply added as powdered limestone, iron ore, and sand, frequently found of sufficient purity where such clays occur. Feldspar is the only practical source of alkali; if the clay is deficient in this constituent, bearing alumina as well, it often imparts too much of the latter to the mixture, when added in sufficient amount to give the required alkali, unless the proportion of the clay be depressed to practical insignificance.

This is the difficulty with the slip-clay used in the above experiments. While the alkali is in itself high, the percentage of alumina is too great, making the former small in proportion to it. The feldspar necessary to bring about a proper ratio of alkali to alumina depresses the allowable proportion of the clay to less than forty per cent. of the mixture, and even in this case the R_2O_3 constituents are high, as they should rather approach 0.5 equivalent, than exceed 0.6.

There is a belief among potters that the glaze produced by the melting of a slip-clay will not "craze" on any body; that other compounds producing glasses are of a nature antagonistic to clays, while slip-clays, being clays themselves, have an affinity for them.

This idea is, of course, quite absurd, as in all cases the perfect union of bodies and glazes is identity of their coefficients of expansion within the limits of elasticity. It is true, however, that the alkali-alkaline-earth glasses allow a greater range of composition of the body between the manifestations of crazing and shivering, than do lead-glasses particularly.

In salt-glazing, as already stated, the body of the ware itself furnishes the necessary alumina and silica for the glaze. The clay should, therefore, contain these elements in proportions most favorable to the production of a hard-fire glaze. As already seen, such glazes approximate a formula

$$1RO\ 0.5R_2O_3 4SiO_2.$$

The yellow-ware clay mentioned in the beginning of the chapter as used for stoneware, although it does not take the salt-glazing well, has the proportion 0.5 R_2O_3 to 2.034 SiO_2. It is therefore too aluminous to take a good salt-glaze.

In the other stoneware clay given, the proportion is $0.5R_2O_3$ to 3.35 SiO_2, which very nearly coincides with what is the best proportion of these constituents in the glazes and accounts for the better formation of the salt-glaze upon it.

One other point, however, also enters into the consideration of the likelihood of a clay's accepting the salt-glaze well, and that is, that it contain sufficient fluxing material to become vitreous at a reasonable heat. For if the clay be still porous when the alkali fumes are introduced into the kiln, these will be absorbed by the ware without glazing its surface.

Recently, the demand for a neater looking interior glaze for stoneware, than the dark-colored slip-glaze has led to the introduction, by a few factories, of whitish semi-opaque glazes. These are of two types, the one being a lead glass, the other an alkali—alkaline earth glass, but both contain zinc oxid as the ingredient giving the distinctive character. One of these analyzed as follows:

	Per cent.
Zinc oxid	13.31
Lime	7.47
Magnesia	0.20
Alkalies	1.56
Insoluble in dilute hydrochloric acid	70.03
Loss on glowing	8.14
	100.71

The insoluble portion:

	Per cent.
Alumina	13.83
Ferric oxid	0.14
Lime	0.60
Magnesia	0.14
Potash	7.47
Silica	47.85
	70.05

This would give a glass with the chemical formula:

$$\left.\begin{array}{l} 0.2335\ K_2O \\ 0.3660\ CaO \\ 0.4005\ ZnO \end{array}\right\} 0.3307 Al_2O_3\ 1.942\ SiO_2$$

1.0 RO

No analysis of sufficient accuracy was obtained of a lead glaze for this purpose. It would appear, however, that in these, 0.2 equivalents of lead oxid substitutes the equivalent of lime and that the silica and alumina are higher.

EXAMINATION OF THE MATERIALS.—The chemical analysis gives the most valuable data for judging both stoneware- and slip-clays. In case of the former, it is necessary to calculate from the analysis the proportions of the equivalent of alumina to silica, in order to see if the clay is likely to salt-glaze well.

The chemical formula of the enduring constituents of a slip-glaze will show at once in how far it will answer the purpose of giving a glass fusible at the heat of melting of pyrometric cone eight, or how it must be modified to meet this end. Still the chemical data must be confirmed by practical burning trials to make certain that the stoneware clays become sufficiently dense, and that the slip-glaze burns brown and not green.

CHAPTER IX.

RAW MATERIALS OF WHITE-WARE BODIES.

various white wares are very seldom made in a "self-body," that is, of a natural white-burning clay, requiring no artificial admixture to enhance the whiteness, increase the plasticity, better the hardness when burned, or modify the coefficient of expansion.

The manufacturer of such ware must, therefore, be well equipped with appliances for washing and mixing the various ingredients of his bodies and he must be better endowed with ceramic skill than the red-ware, yellow-ware, or stoneware potters who accept as bodies the clays furnished by nature, without modification.

The ingredients of white-ware bodies are quite the same as those making up the clays of the commoner kinds of ware, namely clay substance, free silica, and fusible minerals or basic oxids, but they must be as pure as they are severally furnished by nature or as they can be rendered by mechanical means.

The clays required are both primary, china-clay or kaolin, and, secondary, pipe or ball-clay; the former giving whiteness, the latter plasticity to the bodies.

Kaolin or china-clay occurs in considerable quantities and varieties throughout the Appalachian system of the United States, Pennsylvania, Delaware, Virginia, and North Carolina marketing large quantities. Most of that sold is selected, graded, and washed at the mines, by the companies exploiting the same for the pottery industry. Very little is sold in its natural condition.

In perhaps the majority of cases, the kaolinized rock contains the quartz, undecomposed feldspar, and mica, in crystals and laminae of such size that mere stirring or "blunging" of the mineral in water is sufficient to wash out the kaolin, quite free from contamination with detritus of the other minerals. It is recovered by sedimentation and passing the thickened magma through filter-presses.

Still a kaolin may carry a very considerable amount of minerals nearly as finely divided as it is itself. It can be freed from these by a carefully conducted process of floating, though there is in such a case no necessity for separation at all, as these minerals would serve a useful purpose in the pottery body. But it would be necessary to inform the potter, by a careful "rational analysis," what the clay contains so that he may make allowance for the ingredients in preparing his mixtures.

An example of such a kaolin, containing the naturally admixed minerals, so finely divided that they could enter directly in a white-ware body and need not be separated by floating, is that from Nelson County, Virginia, the analysis of which was given on page 10 (Chapter I.).

Another example, striking in the very large amount of finely divided quartz it contains, with very little feld-

spar remaining, is the following. It is unknown from what part of the country the sample came, but its appearance plainly indicated a primary clay.

	Constituents of the entire clay Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	81.11	61.56
Alumina	13.65	0.26
Ferric oxid	0.13	0.00
Lime	0.53	0.18
Magnesia	0.90	0.45
Alkalies	0.91	trace
Combined water	3.59	0.00
	100.82	62.45

RATIONAL ANALYSIS.

	Per cent.
Clay substance	35.47
Feldspathic mineral	1.81
Soluble silica	2.90
Quartz	60.64
	100.82

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	46.94
Alumina	38.12
Lime	0.99
Magnesia	1.27
Alkalies	2.57
Combined water	10.12

The kaolins on the market do not differ widely in chemical composition from nearly pure products, five different brands of well-known domestic china-clays analyzing as follows:

Silica	47.66	48.50	46.47	46.13	45.22
Alumina	37.56	38.31	38.82	39.17	39.11
Ferric oxid	1.39	0.59	0.89	1.00	1.21
Lime	0.20	0.10	0.28	0.22	0.00
Magnesia	0.36	0.14	0.25	0.30	0.28
Alkalies	0.25	0.76	0.48	0.40	0.97
Combined water	13.47	12.24	13.34	13.10	13.20
	100.89	100.64	100.53	100.32	99.99
Insoluble in H_2SO_4 and Na_2CO_3	2.46		0.47	2.54	0.40

Many of our white-ware potters being of English training and using formulas calling for English raw materials, the following analyses of three English china-clays commonly met with in the American market, are given for comparison with our native products:

	Per cent.	Per cent.	Per cent.
Silica	47.96	47.10	48.11
Alumina	38.29	37.33	36.77
Ferric oxid	0.90	1.11	0.44
Lime	0.43	0.14	1.50
Magnesia	0.00	0.47	0.54
Alkalies	0.56	0.20	1.50
Combined water	12.76	13.45	11.80
	100.90	99.80	100.66
Insoluble in H_2SO_4 and Na_2CO_3	0.00	1.24	8.33

The linear shrinkage of china-clays burned to the melting clear of orthoclase feldspar, about the melting-point of pyrometric cone nine, is from four to eight per cent.

They may require as much as forty grams of water for 100 grams dry clay, to make a mass sufficiently soft to allow the Vicat needle to penetrate four centimeters.

CLAY BANK

MUSKINGUM County, O.

Nevertheless the mass of china-clay is of poor plasticity and does not, in the air-dry condition, show a tensile strength of more than 2,000 to 2,500 grams per square centimeter.

The commercial value of a china-clay depends largely upon the whiteness of the body it will produce. Its appearance in the clay state is absolutely no criterion of this, as a clay which is very yellow when unburnt may become very white in the fire. Unfortunately the percentage of iron in china-clays, as shown by their analyses, stands in no direct relation to the tints of the burned products. Nor can a true comparative estimate of the clays be made when they are merely once burned, that is, in the biscuit state. It requires the covering of a thin clear glaze to bring out the true tint.

For the purpose of comparing the tints of china-clays, they must be made up into bodies by the addition of the same proportions of quartz, and feldspar, of the same lot, burned in the same biscuit fire, and covered to an equal thickness with a transparent glaze, which had best not contain over one-half equivalent of lead-oxide, as a glass high in lead is of a yellowish cast, nor should the glaze have been tinted by an addition of cobalt oxide.

To a limited extent, silicates of alumina resembling halloysite, $Al_2O_3.2SiO_2.4H_2O$, have at various times found a local use in place of kaolin.

A clay of this nature from Lawrence County, Indiana, which has had, perhaps, a more extensive pottery-application than any other of this kind, can not be disintegrated by mere washing, but ground in water it gives a very

voluminous mass resembling starch-paste, and is pasty rather than plastic in character, and dries down to a horn-like body. Burned at the heat of running feldspar, it has a linear shrinkage of twenty per cent. from its size in the clay state. The burned clay is much denser than kaolin and has a faintly greenish tint.

Partial analyses of the material analyzed at intervals during a number of years, contained silica ranging from 39.74 per cent. to 41.15 per cent., and combined water from 17.21 per cent. to 17.78 per cent.

An exhibition specimen, analyzed in full, ran much closer to the proportions of kaolin, though with the combined water still high, as follows:

	Per cent.
Silica	44.79
Alumina	38.77
Lime	1.00
Magnesia	0.25
Alkalies	0.67
Combined water	15.49
	100.97
Insoluble in H_2SO_4 and Na_2CO_3	0.98

It is not unlikely that more materials of this nature may be found and applied to special uses in the pottery art. A specimen sent to the writer, as a kaolin from Inyo County, California, appears from the analysis to be of this nature:

	Constituents of the entire clay Per cent.	Portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	44.74	8.99
Alumina	33.23	1.47
Ferric oxid	1.08	0.45
Lime	0.77	
Magnesia	0.23	
Alkalies	2.24	
Titanic oxid	1.10	
Combined water	17.56	
	100.95	10.91

RATIONAL ANALYSIS.

	Per cent.
Mineral and quartz sand	10.91
Clay substance	90.04
	100.95

PERCENTAGE COMPOSITION OF THE

	Clay Substance and Per cent.	Halloysite. Per cent.
Silica	39.70	40.74
Alumina	35.27	34.86
Ferric oxid	0.70	
Lime	0.86	
Magnesia	0.26	
Alkalies	2.49	
Titanic acid	1.22	
Combined water	19.50	24.40

Secondary or plastic clays, known to potters as pipe- or ball-clays, occur plentifully, and of a high degree of purity in a number of the tertiary and quarternary exposures of the country; New Jersey, Florida, western Ken-

tucky and eastern Missouri furnishing the principal supplies.

They are necessary additions to white-ware bodies, because of their plasticity. Being more abundant than kaolins, they are cheaper than these, but are also, even in the best varieties, far less white. Plastic bodies being in reasonable limits easier and hence cheaper to mold, ball-clays are used in as large amounts, for their required clay substance, as the quality of the ware will admit.

From their formation these clays are very likely to contain finely divided quartz and the detritus of fusible minerals, hence their introduction into a body or substitution for some other ball- or china-clay in a pottery recipe, should only be made with a clear knowledge of their chemical composition.

It is, however, a striking fact, that a much larger proportion of the American ball-clays approach the composition of kaolinite, than do those of Europe. The purest of our native ball-clays are mined in Florida, and are being sold as "plastic kaolins," a misleading trade name.

An analysis of one of these runs as follows:

	Per cent.
Silica	45.39
Alumina	39.19
Ferric oxid	0.45
Lime	0.51
Magnesia	0.29
Alkalies	0.83
Combined water	14.01
	100.67
Insoluble in H_2SO_4 and Na_2CO_3	0.87

A sample baked at the melting heat of orthoclase, while very nearly as white as a high grade kaolin, had not at all remained porous, but was dense and glossy, having shrunk fully fifteen per cent. in linear diameter.

Next in purity to these Florida clays are those very extensively mined in New Jersey. An analysis of a typical one of these clays is the following :

	Composition of the entire clay Per cent.	Portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	46.18	3.20
Alumina	39.08	0.39
Ferric oxid	1.11	
Lime	0.42	0.05
Magnesia	0.35	0.05
Potash	0.23	0.05
Soda	0.28	0.21
Combined water	13.04	0.00
	100.69	3.95

Burned at the melting heat of orthoclase the clay was yellowish white and shrank fourteen per cent.

The clay is of good plasticity and requires 51.5 grams of water for 100 grams of dry clay, in order to be penetrated by the Vicat needle.

However, its binding power is very low. Briquettes formed of the plastic clay would not, in the dry condition, bear a strain of more than 1600 grams per square centimeter.

The ball-clays of Western Kentucky and Eastern Missouri, while less pure than the foregoing, are of far greater binding power, giving them, for certain pur-

poses, much the preference over the former. In fact, because of the deficiency of the New Jersey clays, in this particular, not inconsiderable quantities of English plastic clays, that could well be replaced by these western domestic ones, are imported.

A ball clay from Jefferson County, Missouri, of established reputation, has the composition:

	The entire clay Per cent.	Portions insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	48.51	2.85
Alumina	35.18	0.75
Ferric oxid	0.92	
Lime	1.01	0.06
Magnesia	1.47	0.48
Alkalies	2.30	0.35
Combined water	10.72	0.00
	100.11	4.49

Burned at the melting of pyrometric cone nine, the shrinkage of the clay is fifteen per cent., and the body is not only dense from the high contraction and the characteristic structure of the plastic clays, but is vitrified as a direct result of the high percentage of fluxing oxides it contains.

A plastic clay brought into the Market from Calloway County, Kentucky, gave the following analysis:

	The entire clay Percent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	59.83	26.02
Alumina	27.80	0.29
Ferric oxid	0.83	0.07

	The entire clay Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Lime	0.15	0.05
Magnesia	0.24	trace
Alkalies	0.82	0.46
Combined water	10.42	0.00
	100.09	26.89

RATIONAL ANALYSIS.

	Per cent.
Clay substance	73.20
Feldspathic detritus	1.92
Quartz	24.97
	100.09

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	46.19
Alumina	37.59
Ferric oxid	1.03
Lime	0.13
Magnesia	0.32
Alkalies	0.49
Combined water	14.25

At the melting heat of feldspar the clay gives a dense body, but having still some suction when applied to the moist tongue; it is of a yellowish-white color and has a shrinkage of ten per cent.

With the exception of the Florida and some of the New Jersey clays, ball clays are put on the market unwashed.

They almost invariably contain iron pyrites, sometimes in large nodules.

Frequently the more plastic English and Kentucky clays contain sufficient organic matter to appear quite black in their raw state. This may be determined analytically with sufficient accuracy, by dissolving the clay in hydrofluoric and hydrochloric acids on the water-bath, and filtering off the organic flocks on a tared paper, where, after drying, it is weighed. By this method these clays have often yielded the writer as much as four per cent. of organic impurity.

Like the china-clays the ball-clays should be examined comparatively for tint, working them up into bodies with pure flint and feldspar and covering the biscuit pieces with a clear glaze, in the manner already described.

The uncombined silica of pottery bodies, in so far as it is not furnished by the clays in compounding the same, is added in the form of finely ground flint or quartz.

French flints are cheaply imported as ship ballast and used to a considerable extent, though native flint of a high degree of purity is obtainable and also largely used. Flint is roasted previous to grinding, becoming friable through loss of its organic matter. It should burn perfectly white, though a faint pinkish cast is often not objectionable, as the feldspathic flux of white-ware bodies takes up the small amount of ferric oxid producing it, giving a perfectly white sinter.

A native flint of average commercial quality, put on the market by a spar-miller of Trenton, N. J., has the composition :

	Per cent.
Alumina	0.33
Ferric oxid	0.27
Lime	0.13
Magnesia	0.09
Alkalies	0.11
Total impurities	0.93
Moisture	0.24
Silica (by difference)	98.83
	100.00

Heated to the melting heat of orthoclase, it remained snowy white and did not, in the least, sinter together.

A quartz sand, of high purity, mined in LaSalle County, Illinois, which is ground for pottery purposes, has the following composition:

	Per cent.
Alumina	0.155
Ferric oxid	0.069
Lime	0.026
Magnesia	0.013
Alkalies	0.112
Total impurities	0.375
Moisture	0.070
Silica (by difference)	99.555
	100.00

There are, in the country, deposits of silica containing but small amounts of accompanying clay and mineral detritus, that are very finely divided, requiring practically no grinding and burning very white indeed. Such materials are, as yet, not utilized for pottery purposes, though they would furnish an excellent and cheap

substitute for the artificially ground flint, allowance being made in using them, for the clay and fusible minerals which they contain. Being powdered by natural agencies, possibly by precipitation, they seem to combine more intimately with the clays of a mass, making often a more plastic and perfectly knit body, than is obtained with silica reduced by grinding.

A material of this character, from along the Cumberland river in Tennessee, analyzed :

	The entire sample Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	85.80	65.17
Alumina	9.75	0.50
Ferric oxid	0.46	0.04
Lime	0.20	0.08
Magnesia	0.23	0.07
Alkalies	0.98	0.35
Combined water	3.07	0.00
	100.49	66.21

RATIONAL ANALYSIS.

	Per cent.
Clay substance	32.74
Feldspathic detritus	2.94
Quartz	63.27
Soluble silica	1.54
	100.49

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	58.31
Alumina	28.25
Ferric oxid	1.28

	Per cent.
Lime	0.36
Magnesia	0.48
Alkalies	1.92
Combined water	9.37

Baked at the melting-point of feldspar the material has a shrinkage of one and a half per cent., and when it is still porous is much denser than a mixture of a flint and ball-clay according to its rational analysis would become, as a steel point marks but does not scratch it.

Still more striking is a material of this character from Calloway County, Kentucky. Quite friable in its natural state, it hardens somewhat when immersed in water, like a weak plaster. This, however, is very easily ground to a mass which no longer sets. Its analysis is:

	The entire material	The portion insoluble in H_2SO_4 and Na_2CO_3
	Per cent.	Per cent.
Silica	90.49	77.00
Alumina	5.45	0.50
Ferric oxid	0.39	0.02
Lime	0.23	0.03
Magnesia	0.30	0.07
Alkalies	1.74	0.33
Combined water	1.64	0.00
	100.24	77.95

RATIONAL ANALYSIS.

	Per cent.
Clay substance	18.70
Feldspathic detritus	2.71
Quartz	75.24
Soluble silica	3.59
	100.24

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	53.0
Alumina	26.4
Ferric oxid	2.0
Lime	1.1
Magnesia	1.2
Alkalies	7.5
Combined water	8.8
	100.0

Burned at the heat of running spar, the material shrinks but one-half per cent. and is very white. It remains more porous than the material just described and can just be scratched with a knife blade.

Of the fluxes used in the bodies of white ware, feldspar is the most important. It is put upon the market by a number of spar-millers of Connecticut, New Jersey, Ohio, and Pennsylvania of satisfactory purity and of different fusibilities.

A good commercial potash feldspar gave the following analysis:

	Per cent.
Silica	65.85
Alumina	19.32
Ferric oxid	0.24
Lime	0.56
Magnesia	0.08
Alkalies[1]	14.10
	100.15

A commercial soda-lime feldspar, materially more fusible than the former, being sold as a "soft spar," analyzed:

[1] Combining weight, 45.9.

	Per cent.
Silica	66.81
Alumina	21.09
Ferric oxid	0.13
Lime	2.03
Magnesia	0.10
Alkalies[1]	9.64
	99.80

Often the quartz veins of a spar-bed may be difficult to remove or the workmen are careless in picking over the mineral, causing more or less variation of the commercial product, against which the consumer must be on his guard.

Again, it may occur, that the more quartzose portions of a soda-lime spar are ground separately and sold as "hard or potash spar," as was the case with a lot of which the following is an analysis:

	Per cent.
Silica	68.82
Alumina	19.75
Ferric oxid	0.16
Lime	1.64
Magnesia	0.17
Alkalies[2]	9.15
	99.69

It is of about the same fusibility as the true potash-spar shown in the first analysis, and would deceive one in the mere kiln-fusibility test, which is all that potters usually make to verify the quality of the material.

[1] Combining weight, 33.5.
[2] Combining weight, 36.4.

The practical bearing of the difference in composition of these two feldspars of equal fusibilities, is demonstrated in their varying coefficients of expansion—a serious difference if one were substituted for the other in a body having to carry a certain glaze.

This difference is practically shown in the fact that the potash feldspar melted in a thick layer upon a pottery body, cracks off of one upon which the siliceous soda-lime feldspar remains immovably fixed.

Cornwall stone, a partly decomposed granite, mined in Cornwall, England, is used by English potters as their principal pottery flux and also finds considerable application in the United States. All that is used here is imported, no material resembling it having as yet been commercially developed within our borders.

An average sample of a good quality of this material has the following composition:

	The entire material Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	73.57	57.69
Alumina	16.47	4.70
Ferric oxid	0.27	0.30
Lime	1.17	0.10
Magnesia	0.21	0.12
Alkalies	5.84	3.50
Combined water	2.45	0.00
	99.98	66.41
Combining weights of the alkalies	44.6	38.4

RATIONAL ANALYSIS.

	Per cent.
Clay substance and mica	33.57
Feldspar	25.31
Quartz	41.10
	99.98

PERCENTAGE COMPOSITION OF THE

	Clay Substance and Mica Per cent.	Feldspar Per cent.
Silica	47.27	65.55
Alumina	35.04	18.57
Ferric oxid	0.00	1.18
Lime	3.18	0.40
Magnesia	0.26	0.47
Alkalies	6.96	13.83
Combined water	7.29	0.00
	100.00	100.00

The figures show that the kaolinizing decomposition of the rock has proceeded to but a limited extent, the "clay substance," as in this sample, consisting in the main of mica. This is further proven by the constant presence of fluorine, which, though it has been ignored as a separate element in the above analysis, has been found present to the extent of 1.66 per cent.

It may be justified, in the case of this material, in which mica plays nearly as important a part as the feldspar as fluxing constituent, to give it a separate place in the rational analysis, for the better guidance of the potter.

Cornish stone is by no means as uniform in character and composition as potters generally believe.

The portion insoluble in sulfuric acid and sodium carbonate solution is in many cases markedly greater in

alumina than in that of which the analysis has been given and not infrequently the silica is either largely soluble in the sodium carbonate solution or is more readily made so by the action of sulfuric acid than quartz commonly is.

A sample showing both of these peculiarities analyzed as follows:

	The entire material Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	72.99	42.72
Alumina	17.58	7.83
Ferric oxid	0.15	0.10
Lime	1.25	0.71
Magnesia	0.37	0.19
Alkalies	6.20	4.31
Combined water	1.77	0.00
	100.31	55.86

RATIONAL ANALYSIS.

	Per cent.
Clay substance, mica, and soluble silica	44.45
Feldspar	40.68
Quartz	15.18
	100.31

PERCENTAGE COMPOSITION OF THE

	Clay Substance Etcetera Per cent.	Feldspar Per cent.
Silica	68.10	67.68
Alumina	21.94	19.24
Ferric oxid	0.11	0.25
Lime	1.21	1.75
Magnesia	0.41	0.47
Alkalies	4.25	10.61
Combined water	3.98	0.00

The sum of the alkali and combined water in this "clay substance" falls far short of what would be demanded by a mixture of mica and pure clay; while on subtracting the excess of silica, assuming it as uncombined but soluble in sodium carbonate solution, and recalculating the residue on a percentage basis, they assume the proper proportion. This would make the rational analysis:

	Per cent.
Clay substance and mica	25.71
Feldspar	40.68
Quartz	15.18
Soluble silica	18.74
	100.31

The percentage composition of the clay substance and mica then is as follows:

	Per cent.
Silica	44.85
Alumina	37.93
Ferric oxid	0.19
Lime	2.10
Magnesia	0.70
Alkalies	7.35
Combined water	6.88

Direct determinations of soluble silica in a number of such specimens failed to yield anything like the required amount, leading to the conclusion that sulfuric acid may in many cases have more action on some form of silica, in this mineral, as well as in other clays, than that already pointed out in the case of quartz, rendering it in greater measure soluble in sodium carbonate solution.

But more important than the difference in the physical character of the contained minerals or a variation in the apportionment of the elements to the different mineral groups, is the variation in ultimate chemical composition of Cornish stone, particularly in the proportion of the alkalies, as in the following:

	Per cent.	Per cent.
Silica	74.55	73.77
Alumina	17.37	16.05
Ferric oxid	0.26	0.23
Lime	1.68	1.14
Magnesia	0.54	0.22
Alkalies	3.68	7.52
Combined water	2.04	1.78
	100.12	100.71

While Cornish stone has distinct uses determined by its physical properties, it could, in the vast majority of the cases of its application in the United States, be more cheaply and safely substituted by equivalent amounts of native feldspar, kaolin, and quartz, which run much more uniform in quality.

An anomalous material, white, of fine grain, free from crystals of quartz and feldspar, and flakes of mica, resembling a kaolin in appearance, was obtained by the writer from Fayette County, Texas, where it is said to occur in large deposit. It resembles Cornish stone in composition more nearly than any native material which has thus far fallen into the writer's hands.

Its analysis is as follows:

	The entire substance Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	68.88	43.60
Alumina	16.77	7.91
Ferric oxid	0.83	0.32
Lime	0.99	0.26
Magnesia	0.17	0.18
Alkalies	6.77	2.56
Combined water	5.79	0.00
Sulfuric anhydrid	0.42	0.00
	100.62	54.76
Soluble silica (directly determined)	5.23	

RATIONAL ANALYSIS.

	Per cent.
Clay substance	39.83
Feldspathic detritus	40.28
Quartz	14.55
Soluble silica	5.23
Calcium sulfate	0.74
	100.63

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	50.33
Alumina	23.52
Lime	1.03
Alkalies	10.57
Combined water	14.54

The combined water, in this case, seems to belong largely to the soluble silica, which was hydrated so that a portion of it could be extracted with distilled water

alone; but as there was no way of apportioning it, it was counted in with the "clay substance."

This material was substituted for Cornish stone, both in body and glaze trials, with entirely concordant results.

Calcium carbonate, which is much used by the continental potters, finds but very limited application with us as a body-flux.

Commercial whiting is a pure form of this material, as shown in its analysis in a previous chapter, though a higher grade is put upon the market for the use of potters, under the name "Paris white."

Should the manufacture of a ware covered with tin enamels, make a body containing a large proportion of calcium carbonate necessary, such as that used for making the tile of the German and Swiss "Kacheloefen," a cheap and reasonably pure form of this material would be found in the fresh water marls of northern Ohio and Indiana, some of which are now exploited in the production of Portland cement.

Samples of these were found of the following composition:

	Per cent.	Per cent.
Silica	1.16	10.45
Alumina	trace	4.20
Ferric oxid	0.05	trace
Calcium carbonate	94.78	79.35
Magnesium carbonate	0.19	trace
Organic matter and loss	3.82	6.00
	100.00	100.00

CHAPTER X.

WHITE GRANITE AND CREAM-COLORED WARE.

THE bulk of the dishes used for table service and all of those for the toilet and for modern sanitary plumbing, belong to the category of "Granite and C. C." ware. White graniteware or ironstone china differs only from "C. C." that is cream-colored ware and ivoryware, in being made with a larger proportion and better quality of kaolin, so as to be as white in color as possible; the whiteness being generally heightened by the neutralizing of any faintly yellowish cast, through the addition of cobalt-blue to the body and covering the same with glazes in which, among the basic constituents, the alkalies and alkaline earths at least equal or exceed the equivalent of lead. Beyond this, there is no technical distinction between the wares represented by these and some other trade names. Naturally those which are made with less and cheaper kaolin, having a larger proportion of plastic clay, are more easily fashioned, and when covered with a more plumbiferous and hence more fusible glaze, are commoner and cheaper.

The bodies are made mainly from the materials discussed in the previous chapter, their general composition not varying widely from the following:

50 to 60 per cent. clay substance,
38 to 32 per cent. quartz,
12 to 8 per cent. feldspar.

Where Cornwall-stone is used as the flux, its proportion is, of course, larger than that of the feldspar given above and is about such that its mica and feldspathic mineral equal in amount the required feldspar, the additional quartz and clay substance replacing their weight of these in the formula.

The clay substance is made up of kaolin and plastic clay. In the whiter varieties there may be two-thirds of the former to one-third of the latter, while in the more tinted bodies the proportions may be reversed; but in this there is no rule technically imperative, for the tint of body desired, the relative plasticity of the clays, and cost thereof determine the mixture.

If, as is frequently the case, a plastic clay be used, bearing a considerable proportion of quartz, feldspathic mineral, or a clay substance rich in alkalies and alkaline earths, the amounts of added quartz and flux are proportionately less in the body made with it.

The bodies in use have grown up from the most haphazard of empirical trials, but a recalculation of the mixtures, with reference to the composition of the ingredients, will show most of them to fall within the limits of the general formula given. If this be used as the starting point, comparatively few empiric trials would have to be made to attain a body of any desired character, with materials of known composition.

The materials for a body are weighed off in the proportion required, and mixed in the wet way, in the "blunger"

already referred to in the washing of yellow-ware clays.

Errors in the proportions of the constituents entering into the body often occur from the fact that potters, as a rule, are not accustomed to determine and allow for the varying amounts of moisture, which the materials may contain. Thus the powdered flint or quartz will contain from one to four per cent. feldspar, from two to five per cent. china-clays, and Cornish-stone from two to ten per cent., and the various plastic or ball-clays will seldom contain less than ten per cent., and they may often contain as much as twenty-five per cent. uncombined water.

Some of the highly plastic English ball-clays, as also those from western Kentucky, may show in different shipments considerable variation in the amount of contained carbonaceous matter. This should be determined and allowed for, as well as any moisture. Systematic moisture determinations and recalculations of formulas in accord with the results would easily obviate annoying variations in the bodies.

After the mixture has been stirred or "blunged" to a homogeneous slip, this is passed through a revolving, shaking or vibrating sieve covered with a No. 12 silk bolting-cloth or a wire cloth having one hundred and twenty meshes to the linear inch. By this means, such accidental impurities as chips, grain and cinders, which get into the materials from the railway cars, are removed, as also sand and the particularly troublesome small granules of iron pyrites of the ball-clays.

Here, however, is also a point where the composition of the body may materially change. If the slip be too

thick, a considerable quantity of the plastic clay will be taken out of the mixture; but the most important danger arises from insufficient grinding of the fluxes, an appreciable percentage of which may not be fine enough to pass the sieve. This is particularly the case since the introduction of dry- in place of wet-grinding by the sparmillers, and is most to be looked for in the case of Cornish-stone, the tough and flexible crystals of mica, of which resist reduction in pulverizing cylinders much more than they do the crushing and tearing action of the buhr-stones in the wet-drag mills. Cornish-stone has been found on the market leaving as much as fifty per cent. residue on a No. 12 silk bolting cloth, and it is seldom so fine as not to leave five per cent.

As already stated, it is customary, in the case of the whiter bodies, to add a small amount of cobalt, to neutralize any faintly yellowish cast, which they may show. This is usually added in the form of "blue calx," a kind of Thenard's blue, made by roasting a mixture of cobalt oxid with a china-clay and quartz and grinding the resulting mass to great fineness in water.

As the most productive whitening effect and the greatest homogeneity of color is obtained by the most perfect division and distribution of the cobalt, it is better to effect this by chemical precipitation than by mechanical grinding. For this purpose, all that need be done, is to add to the slip a solution of the necessary quantity of a soluble cobalt salt. The natural alkalinity of most waters will be sufficient to precipitate the cobalt perfectly, lodging it on every particle of the charge in

even distribution without spots or specks in the finished body.

Formerly, the useless precaution was taken to pass the slip through a trough in which a row of magnets was suspended, with the idea that iron was to be removed from the clay in this manner; this belief is now practically past and the prejudice against the more convenient wrought-iron blunging tubs and cast iron filter-presses is also fast disappearing.

The body mixed, sifted, and thickened, is fashioned into ware, which is dried and placed in the kiln for the biscuit fire.

The temperature at which this is finished ranges from the melting of pyrometric cones eight to ten; the empiric trials for judging the fire being biscuit rings coated with Albany slip-clay and with feldspar.

The successive changes in appearance of the former material indicate to the experienced eye, the progress of the fire, while the melting of the feldspar determines the finish of the burn.

The properly burned biscuit-ware should be of such hardness that it is not possible to scratch it with a steel point; yet it must be of uniform porosity, it being particularly undesirable for the thin edges and raised points of the modeling on the ware to be so dense as not to adhere when touched to the tongue.

A moderately and uniformly porous body, on being immersed in the creamy liquid of the glaze materials, ground and suspended in water, absorbs the latter, which deposits a uniform coat of its suspended solids on

the surface of the piece. Where, however, this is too dense to take the water up, its solids are washed off, on the withdrawal of the piece from the dipping tub, and after passing through the glost fire these parts appear dry and rough.

The best glazes, for these wares, approach a formula of the following character:

$$\left.\begin{matrix} 0.25\ KNaO \\ 0.50\ CaO \\ 0.25\ PbO \end{matrix}\right\} 0.3\ Al_2O_3 \left\{\begin{matrix} 3.0\ SiO_2 \\ 0.5\ B_2O_3 \end{matrix}\right.$$

$$1.0\ RO \qquad\qquad 3.5$$

A glost-kiln heat approaching the melting-point of gold is usually given, at which the glaze not only runs perfectly bright and smooth but eats itself also slightly into the surface of the body, taking up additionally from the latter a small amount of silica and alumina. Thus thoroughly burned, the glaze should have the coefficient of expansion of a body of a formula lying within the limits of that already given and burned to proper biscuit-hardness. It is also sufficiently bright and of such hardness as not to be scratched by the common table cutlery.

Deviations from the formula given, in the direction of an increase of lead oxid at expense of the lime, and of boracic acid at expense of the silica, and lessening of the alumina and silica occur in many degrees, resulting in relatively more brilliant and easily fusible glazes, but these are also proportionately less white, more easily scratched, and of less range between the crazing and shivering points.

Brilliance is however a consideration in the sale of ware and most glazes will be found rather higher in lead and boracic acid than that of the formula given.

This glaze can, of course, be made in a variety of ways, according to the materials at hand, though the following will serve as a simple example.

Because of the alkali and boracic acid a frit rendering these insoluble must first be made. This is simply done by melting together

0.25	equivalent of	powdered borax,	47.8 parts;
0.5	"	" boracic acid,	31.0 "
0.25	"	" feldspar,	69.6 "
0.5	"	" whiting,	25.0 "
0.5	"	" quartz,	15.0 "

the chemical formula of this frit being

$$\left.\begin{matrix} 0.25\ Na_2O \\ 0.25\ K_2O \\ 0.5\ CaO \end{matrix}\right\} 0.25\ Al_2O_3 \left\{\begin{matrix} 2.0\ SiO_2 \\ 1.0\ B_2O_3 \end{matrix}\right.$$

$$1.0\ RO$$

and its combining weight 141.4.

For the glaze it is then necessary to grind together

0.5	equivalent of the frit,		70.7 parts.
0.25	"	" whiting,	12.5 "
0.25	"	" white lead,	32.9 "
0.175	"	" china-clay,	22.7 "
1.65	equivalents	" quartz	49.5 "

As in the mechanical application of the glaze mixture in a uniform layer to the surface of the ware by dipping the biscuit pieces in the glaze, it is important that its constituents, which differ widely in specific gravity, must remain uniformly mixed and suspended in the

water for a considerable time, the proportion of clay in the glaze mixture, which helps this suspension, should not be too small. It is best, therefore, not to introduce any clay into the frit, but to reserve it unburned for the glaze mixture itself.

Where the amount of alumina required by the glaze is not large it is often best not to introduce feldspar, in order to have all the alumina available for introduction as clay, because of its mechanical use in keeping the glaze materials afloat.

The frit is often melted in saggars in the glaze-kiln. In order to prevent its sticking to the same, it is common to pour out the inner surface of the saggar with a thick milk of flint and water, leaving on the bottom and the walls a coating of flint from one-eighth to a quarter of an inch thick. Into the saggar thus coated the frit mixture is tightly packed. After baking in the glost-fire the saggar is easily broken away from the lump of glass which it contains, and the excess of flint adhering to it is chiseled off. Any remaining too firm for removal is generally too insignificant in amount to affect the composition of the product.

Previous to its introduction in a mill for fine grinding, the frit should be crushed small on a buhrpan under buhrstone runners. Where it is necessary to do this in an iron mortar or between the jaws of a rock- or ore-breaker, the crushed glass must be well freed from the not inconsiderable amounts of fine metallic iron, with which it becomes contaminated, with a large magnet well cleaned of rust.

The mills used for grinding the frit fine are buhrstone drag-mills and porcelain-lined cylinders filled with Iceland flint pebbles. The grinding is done in water.

Far better than melting the frit in saggars, is to melt it on the sloping hearth of a special furnace, from which it can be run through a hole at its lowest point.

By this means the melting is much more thorough. The frit is removed from further action of the fire as soon as it is liquid enough to run from the kiln and it is at once cooled and broken so fine by falling into water that it can be introduced into the fine mills at once.

The gradual and long fire of the glost-kiln is very liable indeed to volatilize alkali and boracic acid from the mixture before they are thoroughly combined into glass, and, furthermore, the slow cooling of the kiln so tempers the latter when melted in saggars, that it is much more difficult to grind than when suddenly quenched in water on flowing from a frit-kiln.

The various materials enumerated in the preceding chapter all enter into glaze formulas. There the composition and properties of flint, feldspar, Cornish-stone, whiting, and the clays have been sufficiently discussed to throw the necessary light on their use in this connection.

The various lead preparations used in glaze making, namely white and red lead, and litharge, are easily obtainable in the market in a high state of purity. The testing of these is also not difficult, and can be found in books on technical analysis.

It remains merely to call attention to a superstition among potters, created by commercial rivalry among white-lead manufacturers, that traces of acetates in white

lead are of deleterious influence on the glaze. A real danger lies in the mistaken or ignorant use of lead sulfate in the place of white lead. This sulfate is now produced by direct oxidation of galena and put upon the market under names tending to confound it with the former product.

Borax is obtainable of sufficient purity, though it is usually well to examine it for the possible presence of sodium sulfate.

Boracic acid may contain ammonium sulfate and prove troublesome by introducing sulfates into the frit. As much as 10.28 per cent. SO_3 has been found by the writer in the light-brown flaky variety.

Soda is more conveniently employed in the form of soda-ash, as the large amount of water of crystallization in sal-soda is troublesome in the melting of a frit containing it, and furthermore the efflorescence of the salt, when standing in open barrels is liable to cause serious changes in the composition of mixtures made with it.

It is important to examine all soda-ash for the presence of sulfate. That made by the Solvay process, and now becoming common in the market, is free from such contamination however.

Potash, where its introduction as potash-feldspar is not admissable, because of the amount of alumina or silica necessarily accompanying it, is used as pearl-ash, or where great purity is required as bicarbonate or nitrate.

On account of its variable composition pearl-ash should always be subjected to chemical analysis previous to use and because of its hygroscopic character, its moisture should be determined and allowed for whenever it is applied.

CHAPTER XI.

MAJOLICA AND ENAMELED TILE.

WITH exception of the printing and hand painting in vitrifiable colors and gold, and, to a more limited extent, in underglaze colors, on the useful articles of manufacture coming under the head of the kinds of ware described in the last chapter, the principal commercial development of ornamental pottery in the United States has been in the use of transparent colored glazes on modeled surfaces.

In so-called majolica, of which many articles of an ornamental and semi-useful nature are made, a decorative effect is sought to be attained by the application of differently colored glazes to different parts of the piece. The colored glazes are put on thin, and the ware is generally very imperfect technically, the glazes being minutely crazed and the body very porous and brittle.

In enameled tile the individual pieces, modeled as a rule in bolder relief than the ornament of the former, are colored in monochrome, through a very heavily glazed surface. The decorative effect being attained by the variation in depth of the glaze through the approach to or recess of the contour of the design from the surface of the glass, lighter and darker tints of the color appear and bring out the design in light and shade.

To a certain extent also, mottled colors in imitation

of marbles are used, but in all cases the decorative effect sought is dependent on the thickness of the glaze, which in such measure refracts the light and makes the glaze brilliant.

This ware, manufactured and used very extensively for interior decoration in kitchens, halls, bath rooms, about hearths and mantel pieces, is artistically as well as technically much better than that previously mentioned; but the heavy glazes employed to make it decorative, offend good taste as well as make it practically impossible in manufacture to steer the product uniformly perfect through the "Scylla and Charybdis" of crazing and shivering.

The body and glazes of both of these kinds of ware are very much the same. The former coincides in composition with the body of cream-colored wares, but is as a rule not so hard, because the manufacturers of ornamental articles are more careless in the giving of a thorough biscuit fire, than those who are faced with the conditions imposed on useful products.

Tile, which must burn perfectly level and true in size and shape, are not formed from the mass in a plastic state, but this is dried and reduced to a powder containing from eight to ten per cent. moisture, which is pressed into shape in metal dies with powerful screw, cam, or hydraulic presses.

By this means, bodies are obtained that are little liable to warp or become otherwise untrue in drying and burning, but the clay particles not being nearly so closely bonded as in drying down from a plastic condition, the

larger pieces are with many clays subject to cracking or "dunting" as it is called. In addition to the other conditions that obtain in mixing white pottery bodies, this danger must be kept in mind in selecting a body suitable for tile.

The clear glazes used as the bases of the colored ones, for these industries, are both raw and fritted. The former resemble closely those used in yellow ware; the latter must be more fusible and brilliant than those employed for white granite and cream-colored wares and contain, therefore, more lead oxid and boric anhydride and rather less silica and alumina.

However, the tints imparted by the chromogenic oxids to glazes are so profoundly influenced by their chemical composition and the relative proportions of their basic and acid oxids, that the widest divergence in composition must be looked for.

It is only possible, therefore, to give for illustration a common type of a good glaze of this class, as the following:

$$\left.\begin{matrix} 0.25\ Na_2O \\ 0.25\ CaO \\ 0.50\ PbO \end{matrix}\right\} 0.2\ Al_2O_3 \left\{\begin{matrix} 2.5\ SiO_2 \\ 0.5\ B_2O_3 \end{matrix}\right.$$

1.0 RO

It may be prepared by first melting a frit of

0.5	equivalent	borax,	95.5 parts.
0.5	"	whiting,	25.0 "
2.0	"	flint,	60.0 "

its formula being

$$\left.\begin{matrix} 0.5\ Na_2O \\ 0.5\ CaO \end{matrix}\right\} \begin{matrix} 2.0\ SiO_2 \\ 1.0\ B_2O_3 \end{matrix}$$

and its combining weight 124.5. In order to make the glaze it is then necessary to grind together

0.5 equivalent of the frit,			62.25 parts.
0.5	"	" white lead,	64.85 "
0.2	"	" china clay,	25.9 "
1.1 equivalents	"	flint,	33.0 "

For coloring the glazes, cobalt, nickel, copper, chrome, manganese, uranium, and iron oxids are in use.

It is customary to grind these with quartz and china-clay previous to their addition to the glaze, in order to insure their perfect division, that they may dissolve in the glazes without producing spots of deeper tint, but produce a uniformly colored glass. As a rule there is no proportion of these admixtures bearing any rational relation to the glazes that is observed; in fact, the only thought connected with this addition, beside that of division of the coloring oxid, is cutting down its tinctorial power, so that those of higher coloring property receive the larger additions. As a result, the addition of these colors changes the formula of the glaze to a greater or less degree. It would, therefore, be a more rational proceeding to add to the various oxids, in grinding the corresponding colors, the quartz and china-clay in such proportion as to give compounds of the same acidity as the glaze in which they are to be used. Any desired proportion could then be added to the glaze without materially disturbing the relations of its chemical formula, which is of some moment both with reference to the fusibility and the coefficient of expansion. Such mixtures, for the above glaze, would be composed as follows:

For cobalt color

1.0 equivalent	cobalt oxid (Co_3O_4),	40.0 parts.
0.2 "	china-clay,	25.9 "
2.6 equivalents	flint,	78.0 "

and for the other colors, like amounts of clay and flint, with the following amounts, respectively, of the oxids:

37.4 nickel oxid (NiO).
39.8 copper oxid (CuO).
38.3 chromic oxid (Cr_2O_3).
38.2 manganese oxid (Mn_3O_4).
40.0 ferric oxid (Fe_2O_3).
70.7 uranium oxid (U_3O_4).

A better method than this, insuring the most perfect division of the coloring oxid and no disarrangement of the chemical formula of the glaze by its addition, is to substitute the oxid for one-half of the basic equivalents of the glaze formula and melt the resulting mixture. A series of colored frits, each containing one of the coloring oxids in definite chemical proportion can thus be made, which may be added in any desired measure, to the clear glaze, in order to produce the various colors. The formula of these colored frits would then be, for the clear glaze given

$$\left.\begin{matrix} 0.125\ Na_2O \\ 0.125\ CaO \\ 0.25\ PbO \\ 0.50\ RO \end{matrix}\right\} 0.2\ Al_2O_3 \left\{\begin{matrix} 2.5\ SiO_2 \\ 0.5\ B_2O_3 \end{matrix}\right.$$

The different coloring oxids take the place of RO. Thus, the copper frit would be made by melting together the mixture:

0.125	equivalent	powdered borax,	23.9	parts.
0.125	"	whiting,	6.25	"
0.25	"	white lead,	32.4	"
0.5	"	copper oxid,	19.9	"
2.1	equivalents	flint,	63.0	"
0.25	equivalent	boracic acid,	15.5	"

This would yield 135.7 parts of glass, that are then ground with 0.2 equivalent of china clay, 25.9 parts. In the other frits the copper is replaced by the equivalent weights of the respective coloring oxid.

As these frits are used in small amounts, melting them on the hearth of the frit-kiln would not be practical. The advantages of the frit-kiln on a small scale can be attained, however, by melting in large crucibles, pierced in the bottom with a hole three-eighths of an inch in diameter. As many of these as frits are desired to be melted at one time, are placed side by side on the flat hearth of a furnace having a hole two and one-half inches in diameter under each crucible. Into each of these, which must be easily reached and filled from above through corresponding openings in the crown of the furnace, its frit-mixture is introduced, which on becoming sufficiently fluid, runs from the hole in the bottom, falling through the opening in the hearth, into a suitable receptacle filled with water below.

The principal raw materials of these glazes, with exception of the coloring oxids, have been previously discussed. Cobalt is commonly met with in the market as black oxid, prepared for use in Saxony and Wales. All commercial preparations contain nickel oxid in larger or smaller proportion, as the impurity affecting the tint of

the glass in which the oxids are used. The amount of nickel oxid contained in the Saxon brands R. K. O. and F. K. O. is from five to six per cent.; in G. K. O. there is from two to three per cent., and in F. F. K. O. one-half per cent.

The Welsh oxid, seen in this market, generally contains about five per cent. nickel oxid. Nickel oxid itself is not used very extensively from the fact that in the more convenient glazes, which are rich in lead oxid and boracic acid, it is very liable to cause turbid loam-colored separations, and to shade badly from brownish to greenish tints. It is, however, serviceable in the more alkaline glazes and those poor in boracic acid.

Nickel oxid is obtainable quite pure of domestic manufacture.

Copper oxid in the form of copper scale or black oxid, is of such varying origin as found in the market, that it is advisable to always subject it to examination previous to use. As only glasses containing lead oxide in at least some proportion are in use, and the glost-fire is of necessity oxidizing only the green and blue-green tints of the oxid are known in our domestic pottery. The sub-oxid supplied to glass makers for ruby glass, finds no application.

Chromic oxid is very commonly made by the potters themselves, by roasting an intimate mixture of potassium bichromate and sulfur in the top-kiln or flue of the glost-oven, and grinding and washing the product until free from alkaline sulfid. Used in larger proportion, chromic oxid produces intransparent green enamels, and even in smaller amounts it is liable to separate from the clear

greenish-yellow glass in deep green intransparent flecks. It is frequently the custom, therefore, because of the better division of the oxid, to introduce it in the form of mercuric chromate or lead chromate. The latter should never be used without previous examination, as it is manufactured mainly as a pigment, and as such is frequently adulterated to render it lighter in tint.

Manganese is an important chromogen for pottery glazes and is used in several forms. Where brown tints are desired, the presence of iron oxid is not only not objectionable, but is needed, the amount depending upon the required tint. The most common form in which manganese finds application is as black oxid or pyrolusite. It is sold in a variety of grades, varying considerably in the amount of contained sandy matter and ferric oxid, so that where exact and economical work is contemplated, it should always be analyzed before use. Where yellowish-brown tints are required Turkey umber is often employed, though its use is neither economical nor rational, inasmuch as the color imparted by this substance is due to the contained manganous and ferrous oxids. It would be better and cheaper to add these substances in approximately pure form, as commercial umber varies considerably in the percentage of these present. Nor is it graded, commercially, so that one could form a rough idea of the proportion of its important constituents; for being mainly used as a pigment, physical rather than chemical properties determine its grade.

Umber usually contains from sixteen to twenty per cent. of manganous oxid and from thirty to thirty-eight per cent. ferric oxid. It generally contains also quite

an appreciable amount of gypsum, which is objectionable on account of the introduction of sulfates into the glaze.

Where the reddish and wine-colored tints of manganese are desired, it is essential to use preparations entirely free from all traces of iron. In this case it is common to use manganous carbonate. It is important, however, not to trust commercial preparations, which often contain as much iron as common pyrolusite. Not infrequently the commercial carbonate contains considerable amounts of calcium carbonate, not intentionally added, but derived probably from a recovered manganese.

The following analyses are of preparations of this character:

	Per cent.	Per cent.
Sandy matter	0.10	13.17
Alumina	0.11	
Manganous carbonate	52.15	63.17
Calcium carbonate	47.07	21.55
Magnesium carbonate	0.57	2.11
	100.00	100.00

As pure manganous carbonate is by no means a stable product, but loses moisture and carbonic acid on exposure to the air, it should be assayed from time to time, or it should be converted, by heating in the presence of air, into mangano-manganic oxid and weighed as such.

Uranium is offered in the market as oxid, ranging in color from a bright canary to an orange-yellow. The preparation is really a hydrate, and a difference of five per cent. in the amount of loss on glowing different specimens under similar conditions has been found by the writer. The colors obtained with uranium vary with the composition of the glaze from greenish lemon-

yellow to orange. The black color imparted to certain fluxes, used in the vitrifiable colors of overglaze painting, is not producible in the glazes and under the firing conditions of pottery. Pitch-blende, used by European potters, is not known to those of the United States.

Ferric oxid is a useful chromogen, giving orange and brownish-yellow tints. It is readily obtained of sufficient purity, but being mainly prepared for the market as a pigment or polishing powder, physical properties determine its commercial grading and the higher priced samples are often the poorest for the potter's use. Ferric oxid should never be used, therefore, without previous chemical examination.

Specimens prepared directly from hematite and other iron ores generally contain more or less sandy matter; those made by roasting copperas often contain injurious residues of sulfuric acid.

The crocus powders to which potters are particularly partial, as most English pottery receipts call for "crocus martis" in place of ferric oxid, are treacherous because of the foreign additions they almost invariably contain, which have been added to brighten the color or improve their character as polishing agents. A "crocus martis" sold to a pottery was found by the writer to contain:

	Per cent.
Ferric oxid	47.14
Alumina	2.31
Silica	13.65
Barium sulfate	37.41
	100.51

Underglaze crimson is used instead of copper and gold for pink and red glazes, the colors being much more easily obtained, though far inferior in quality to those producible with the latter agents. The color consists mainly of stannic oxid, containing a trace of chrome in minute division. The analysis of a good quality of the color of English manufacture ran as follows :

	Per cent.
Silica	10.02
Alumina	1.57
Chromic oxid	strong trace
Lime	20.32
Carbon dioxid	1.00
Stannic oxid (by difference)	67.09
	100.00

Colors with increased lime and a reduction of silica impart a disagreeable purplish cast to the glaze. The composition of the latter also affects the tint considerably ; boracic acid, particularly, can only be used in small proportion.

Stannic oxid is used to convert the clear glazes into white intransparent enamels. As its effect depends upon its being insoluble in the glass, and clouding it by remaining suspended in it, its physical character is all important. Many commercial preparations of the oxid are much too dense, collecting in little concretions in the glass and giving it a curdy appearance without much covering power.

To insure a perfect division of the tin oxid in the glaze it is best to introduce it in the form of a "putty-

powder," with the lead oxid. This is done by first preparing an alloy of the metallic lead and tin and carefully oxidizing it in a flat pan or on the open hearth of a furnace, with plentiful excess of air, raking off the oxid from the surface of the molten metal as it forms.

The oxid is then ground in water for a short time in a tumbler mill and floated from the flattened grains of unoxidized metal.

The dried powder must be assayed and its addition to the glaze regulated by its proportions of the respective oxids.

CHAPTER XII.

WHITE ENAMELED BRICK.

THE development of fire-proof building has made a permanently white covering for walls, imperative as a substitute for lath and plaster. The light-conditions of our large buildings in crowded city quarters, demand that this covering be highly reflecting, easily cleaned, and as permanent as the structure itself.

Answering these and many minor conditions, brick with one or two faces covered with a white glazed or enameled surface are being supplied to meet the demand for such walls for ware-cellars and subways, the halls and corridors of public buildings and railway depots, the operating rooms of hospitals and light-shafts and light walls of the narrow courts of office buildings.

The technical condition of the manufacture of these brick, namely the melting of a solid enameled surface on a bulky ware of coarse clay, together with the cost of frequent and careful handling, has presented such difficulties that the manufacture has not kept pace with the demand; hence a large portion of the supply comes to us from abroad.

The methods of making these brick are two. The one consists in covering the surface to be exposed, with a tin enamel of sufficient covering power to present a

smooth white surface completely concealing the clay underneath; the other, in coating the face to be exposed, with an engobe or "slip" of china-clay or of a body resembling that of white ware and melting a transparent glaze over this.

Where the character of the clay is such that it can be burned at the same heat as the glaze or enamel it will bear, the aim is to finish the piece with its coating in the clay state and subject the product to but one fire.

Tin enameled brick are best made on the plan of the white stove tile used on the continent of Europe. For these, clays rich in the carbonates of lime and magnesia are best suited. The enamel will lie on them as a smooth and uniform glass without danger of beading up and leaving portions of the surface uncovered, and if the carbonates be present in sufficient amount, without crazing. Such clays should bake to the hardness of good building brick at silver-melting heat, which is the best temperature for flowing the lead-tin enamels.

As a type of such clays, burning to a light buff color and of sufficient hardness at the melting-point of silver (960° C.), one from Hamilton county, Ohio, may be taken, which gave the following analysis:

	The entire clay Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	41.66	25.50
Alumina	10.93	2.03
Ferric oxid	5.00	0.00
Lime	15.77	0.17
Magnesia	6.27	0.15
Potash	2.15	0.53

	The entire clay Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Soda	0.50	0.31
Carbon dioxid	13.24	0.00
Combined water	3.88	0.00
	99.40	28.69

This would bear an enamel of German manufacture, very white, of excellent covering power and entirely fritted, that analyzed as follows:

	Per cent.
Lead oxid	28.56
Stannic oxid	9.40
Alumina	4.79
Ferric oxid	0.08
Lime	0.60
Potash	8.82
Loss on ignition	0.93
Boracic acid	none
Silica (by difference)	46.82
	100.00

The chemical formula of the glass then is:

$$\left.\begin{array}{l} 0.5511\ PbO \\ 0.4029\ K_2O \\ 0.0460\ CaO \end{array}\right\} 0.2035\ Al_2O_3\ 3.358\ SiO_2$$

1.0 RO

with 9.4 per cent. suspended SnO_2.

But tin-enameled brick made with calcareous clays and finished in one fire are not yet common in the United States. In most cases the enamel is applied to ordinary buff and even red brick and flowed in a second heat.

A brick of American manufacture was found by the writer, which did not quite conform to either of the above. The enamel had been applied to the "biscuit" or once baked body, but between the brick proper and the enamel was an engobe, apparently applied for the twofold purpose of helping to conceal the body, as the enamel in itself seemed of insufficient covering power and for supplying a surface to which the enamel would adhere without beading and crawling, as the body of the brick contained insufficient lime to insure this.

The material of the brick consisted of

	Per cent.
Silica	67.99
Alumina	24.97
Ferric oxid	1.12
Lime	3.63
Magnesia	1.46
Alkalies	1.24
	100.41

The enamel carefully dressed from the surface gave the analysis:

	Per cent.
Stannic oxid	11.42
Lead oxid	33.11
Alumina	7.86
Lime	4.53
Magnesia	0.36
Alkalies	4.87
Boracic acid	none
Silica (by difference)	38.85
	100.00

the chemical formula of the glass then being:

$$\left.\begin{array}{l} 0.1798\ K_2O \\ 0.3037\ CaO \\ 0.5165\ PbO \end{array}\right\} 0.2654\ Al_2O_3\ 2.252\ SiO_2$$

1.0 RO

with 11.42 per cent. suspended SnO_2, though so poorly divided that the enamel looked curdy and was, as already stated, of poor covering power.

The alumina, as found by the analysis, is unquestionably higher than was originally introduced in the glaze; but in fusion some would be dissolved and taken up from the surface of the body or engobe beneath. Taken as the analysis shows it, the enamel would be produced by the following formula:

0.5165	equivalent	white lead	66.98 parts.
0.3037	"	whiting	15.20 "
0.1798	"	feldspar	50.08 "
0.0856	"	china clay	11.10 "
1.0000	"	flint	30.00 "
		Tin oxid	19.86 "

The engobe was so eaten into by the glaze that it was difficult to chip off a pure specimen. The best that could be obtained was of the following composition:

	Per cent.
Silica	44.56
Stannic oxid	2.75
Lead oxid	25.22
Alumina	19.50
Lime	0.57
Magnesia	2.10
Alkalies	5.30
	100.00

Taking the stannic oxid, in the above, as indicative of the amount of enamel present in the specimen analyzed and deducting the proportionate amounts of the other constituents, the engobe proper must have had (in the burned condition) the percentage composition:

	Per cent.
Silica	46.51
Lead oxid	22.79
Alumina	23.27
Lime and magnesia	1.97
Alkalies	5.46
	99.99

which would approximately be given by the mixture:

Feldspar	50 parts.
White lead	25 "
China-clay	33 "

The other type of "enameled" brick mentioned, having a clear glaze over a white engobe which covers and conceals the buff-body of the brick, is made from a sandy fire-clay and finished with its two coatings in the clay state, being subjected when dry to but one fire. The temperature of this is quite high, sufficient to melt the pyrometric cones nine or ten, the glazes used not being plumbiferous, but of the porcelain type.

The body of an English brick of this character had, in its burned condition, the composition:

	Per cent.
Silica	72.36
Alumina	24.97
Ferric oxid	0.74
Lime	1.34

	Per cent.
Magnesia	0.30
Alkalies	1.01
	100.72

The engobe was a pure china-clay. The glaze was composed of

	Per cent.
Silica (by difference)	66.67
Alumina	20.64
Lime	7.68
Magnesia	0.33
Potash	4.68
	100.00

its chemical formula being

$$\left.\begin{matrix} 0.26K_2O \\ 0.74CaO \end{matrix}\right\} 1.04Al_2O_3.\quad 5.76SiO_2.$$

In the severe fire, to which the ware has been subjected, the glaze has, of course, taken up alumina and silica from the engobe, so that its original composition would not accord, in the proportion of these elements, with the formula derived from the analysis of the fired product, as above given. A comparison of this formula with those of the stoneware slips, shows by how much approximately the proportions of alumina and silica are perhaps too high.

The formula as it stands would be produced by the following mixture :

0.26 equivalent feldspar	72.41	parts.
0.74 " whiting	37.00	"
0.78 " china-clay	101.01	"
2.64 eqivalents flint	79.02	"

Trials made on the basis of the above formula with systematic reduction of the china-clay and if need be of the flint, would in a very few trials give the composition of a glaze such as a particular clay and the fire required to bake it would need.

The clear glaze chipped from a brick of similar character of American manufacture gave the analysis:

	Per cent.
Silica (by difference)	65.67
Alumina	20.20
Ferric oxid	0.49
Lime	6.27
Magnesia	0.88
Alkalies[1]	6.49
	100.00

the chemical formula then being

$$\left.\begin{matrix} 0.3544K_2O \\ 0.6456CaO \end{matrix}\right\} 1.01Al_2O_3.\quad 5.53SiO_2.$$

1.0 RO

The adaptation of a clay and enamel or of a clay, engobe, and glaze to each other, in both of these kinds of brick, involves considerable empiric experiment, particularly if it is aimed to finish them in one fire. Not only do the difficulties due to differences of their coefficients of expansion arise, causing crazing or shivering of the glaze or enamel which must be avoided, but also the shrinkage conditions in the clay state must be so met that the surface coverings do not shell off in the drying or loosen so as to turn up in the fire, melting back in

[1] Combining weight, 46.3.

beads with exposure of uncovered patches of the brick surface.

A consideration that has received very little attention thus far, but is of considerable moment, is that the glaze or enamel itself must resist all action of the atmosphere and the body of the brick should be of such density that the combined action of moisture and frost does not cause the white coating to split off. The majority of the brick now placed, it is true, are not subjected by their position to the latter danger, but it is not unlikely that in time an important use will be the facing of the walls of light courts, which are not under roof.

The glazed surface cannot, in itself, be depended upon for preventing the rain-water from penetrating the brick, as it would find ample access to the body of the same through the mortar-joints. From such brick, saturated with water and subjected to several frosts, the impervious surface not allowing the expansion of the ice through absence of pores, is very soon pushed off. Hence, glazed or enameled brick, in order to be of prime quality, should be very nearly vitreous in body. It is, of course, out of the question to attain this with the soft-fired calcareous body of the first type and these brick should only be used for interior work. A specimen of the kind described, having a feldspar-lead china-clay engobe between the body and the tin enamel, absorbed eighteen per cent. of water. It showed cracking and loosening of its enamel when saturated with water and frozen and thawed twice. In five freezings and thawings it was completely ruined.

Brick of the second type with even a porosity allowing an absorption of five per cent. of their weight of water, withstood thirty freezings and thawings, without damage to the coated surface. There are few brick of even this type in the market, whether of foreign or domestic manufacture, as dense as this. Most of them will take up ten per cent. by weight of water, which is too much for safe out of door exposure.

The hard alkali-alkaline earth glazes are far the best for resisting atmospheric influences, but even lead glazes and enamels, if of suitable composition, may be relied on for retaining a bright reflecting surface.

In order to test if such glazes are in no danger of suffering surface decomposition, in the course of time, by the action of moisture and carbon dioxid, the most rapid and practical method is that of Professor Rudolf Weber. The glazed surface is exposed for twenty-four hours under a bell jar to the fumes of highly concentrated hydrochloric acid. Dried in an atmosphere free from dust, the surface must remain perfectly bright or show at most the very faintest clouding. Marked clouding indicates a decomposition of the surface, which may be further seen on wiping off the cloud of salts and separated silica in a decided iridescence of the glass.

CHAPTER XIII.

FLOOR-TILE AND TERRA-COTTA.

THE raw materials of the unglazed wares for architectural use and ornament are almost coextensive with the argillaceous minerals of the earth. Their final selection for the several purposes depends upon the conditions of use and upon the necessary or accidental conditions of manufacture.

The first considerations are with reference to physical properties, allowing facile shaping and the faultless drying and burning of the ware.

In plastic-formed objects, particularly in very large pieces of architectural terra-cotta, the degree of plasticity and the binding property of the clay are matters of very great moment, which in the present state of knowledge can only be safely determined empirically and on a scale of actual work.

The plasticity of the clay must be ample to allow for the easy forming of the mass in molds, or its modeling free-hand, and also allow heavy masses in bold relief to sustain their own weight. Yet the clay dare not be so plastic that it be strained in the shaping and twist and be contorted in drying and in the fire. To a certain degree the evils of an over-plastic and a very fine grained material are overcome by adding once fired clay ("grog") in coarse grains to the mass.

Such material must have sufficient binding property to resist, without cracking, the strain of a shrinking surface on a less shrunken interior, during the operations of drying and burning,—both attended by appreciable reductions of mass from the surface inward.

Dust-pressed ware, such as flooring tile and molding brick for belt-courses, require a material that does not form center-cracks, from the surface-sealing of the clay during pressing, before the air contained in the powder has escaped, a phenomenon known as "busting." The material must further allow the ware to dry and be burned without warping, cracking through ("dunting") or becoming covered with surface-cracks ("checking").

The selection of a proper kiln-temperature for burning the ware is a difficult matter that can also only be done empirically. As a rule in these manufactures a variety of colors are required and the problem of temperature is the finding of the heat that will bake to proper hardness the largest number of the available clays, so that by mixing and suitable disposition in the kilns, as great a variety of colors as possible may be burned in one and the same fire.

The temperatures employed in these industries vary from that of the melting-point of silver to that of pyrometric cone ten. As a rule, too, they have been derived haphazard from the heat found best for one clay and one particular kind of ware and not from systematic trial of all the clays that are likely to enter into the manufacture. As a result many establishments labor under the serious difficulty that a part of their products are far less perfect

than others, because the whole are burned in the same fire, which is only suited to ware from one or two of the clays. Or, again, in order to meet this difficulty, the colors which can not be properly produced from the local clays at the established temperature, must be gotten from clays obtained from a distance, thus burdening the manufacture with great expense.

The conditions thus imposed by chance are in the majority of cases accepted as inevitable to the manufacture and no systematic effort is made to readjust and correct them.

While it is true that mere analyses of materials are of little or no avail in the solving of such problems, the training of the technical chemist fits him better to carry out systematically the many empiric trials necessary for the readjustment of the conditions or their proper establishment originally in these works. The opportunity afforded workers of such training, to study the problems of these arts in actual manufacture, will alone lead to the finding of physical data, obtainable in the laboratory, by which the behavior of the various clays can be foretold and bases of rational manufacture worked out before the practical establishment of plants.

All wares for architectural use must adhere closely to definite sizes. The shrinkage of the clays employed must therefore be definitely known for the temperatures to which they are to be subjected, so that the molds and dies can be made of the proper dimensions. Frequently pieces of the same pattern, but of different colors, alternate in a frieze or floor. It is therefore a great conveni-

ence if the shrinkage of all the adopted colors be adjusted to the same scale, as it would save carrying molds and dies of the same design in a variety of sizes. The question, however, is entirely one of convenience and relative expense. In the case of dust-made brick with plain and simple molding faces and geometric floor tile, it is perhaps best that the bodies employed have different shrinkages; as in that case the dies, after wearing too large for the material of least shrinkage, can be chopped out to the size required for the clay of next greater shrinkage, and so continue until they have done service for the entire color scale. Were all the materials on the same scale of shrinkage, the life of a die would be comparatively short, as it could no longer be used when it became too large, by wear, for the standard size.

The question of shrinkage is most aggravated in the case of encaustic tile, whether made plastic or of dust-clay. In these, the colored clays forming the design are inlaid in the clay making the body of the ware. As the product must be absolutely level, the least difference in the shrinkage of the several clays, both in the drying and burning, would unfailingly warp the tile, either causing them to "buckle" or "dish." In this manufacture it is also absolutely necessary that each colored clay require the same heat and attain an equal hardness with the others, for it must be possible to inlay any combination of the color scale into the same piece, and therefore occupy the identical position in the kiln. Advantage, therefore, cannot be taken of the greater or less difference in temperature that always exists between

certain parts of a kiln, for burning particular colors, as is always done, where individual pieces are made of but one mass.

Soluble salts of the alkalies, alkaline earths, or of iron, whether pre-existent in the clay or formed while it lies as a damp mass or in the fire, are dangerous in a variety of ways; chemical examination for their presence or the likelihood of their formation, is an important though greatly neglected step in the selection of clays, for ware which is not to be glazed.

Gypsum, if present, and ferrous sulfate often formed in the damp clay by oxidation of the finely divided iron pyrites it may contain, are on the drying of the finished pieces brought to the surface, particularly on prominent points and ridges, where, on account of the readier evaporation, larger quantities of the contained moisture with its dissolved salts, are drawn by capillarity. Thus, on the eye-brows, tip of the nose, lips, and chin of a terra-cotta head would most of the salts be lodged. On burning, these surfaces, which in the clay state may have shown no defect, become bodily discolored; red and similar colors will, through the presence of lime salts, become buff, and where there are larger amounts may be even coated with a whitish, irremovable scum; while light-colored clays would, through the presence of the iron salts, stain brown in these parts.

Where the use of such clays cannot be avoided, two methods of treatment are employed to escape these results. One consists in adding to the clay barium chlorid and carbonate, in order to render the salts insoluble by

double decomposition, preventing their carrying to the surface with the movement of the water in drying. Eighty-five to ninety per cent. of the barium necessary, as shown by the determination of sulfuric acid in the clay, is added in the form of chlorid, dissolved in water, and the remainder with a small additional excess, in the form of carbonate. The other method consists in preventing evaporation from the right side of the ware, by coating it, after it has been formed and finished, but before drying, with crude petroleum or tar. As the evaporation is forced to take place entirely from the uncoated surfaces, the salts are, in the drying of the ware, entirely carried away from the surface and lodged where, in the setting of the piece in the wall, they are unobjectionable. The coating material of the face must be of such a nature that it burns away without leaving a blemish. In the case of ware burned at higher heats and not protected from the immediate contact of the flame, surface discolorations are likely to occur from the flying ash of the firings. Where this is a matter of serious objection, it is necessary to burn with fuel gas or crude petroleum, or at least with a solid fuel containing less iron than the ash of our commoner coals. Where the temperature reached is not so great as to destroy the sulfates of the clay and fix their bases as undecomposable silicates, or where the burning is conducted with fossil fuels, containing sulfur, with a practically continuous oxidizing flame, so that the clay takes up sulfuric anhydrid from the fire gases, soluble salts are lodged in the ware. These tend seriously to deface it if, as in

the case of bricks and terra-cotta, it is exposed in outer walls to alternate damp and drying. Through these processes the salts are brought to the surface as a white crystalline efflorescene in dry weather, which is not washed off but returned by absorption to the ware with the first succeeding rainfall. The efflorescences, consisting mainly of potassium, calcium, and magnesium sulfates, cannot be removed except by scraping the surface after a period of drought has brought them thoroughly out of the body of the ware. It is then possible, by careful application of a dilute solution of barium chlorid, to fix what still remains in the body of the wall.

All the efflorescences of salts found on walls are by no means derived from the brick or terra-cottas alone. Frequently the mortar or cement setting is responsible; often in stables or outhouses, where nitrogenous liquids are absorbed by the brick or ammoniacal fumes are plentiful, the ware may be the seat of a true nitrifactive process and the salty efflorescences contain considerable nitrates.

Soluble lime salts may be introduced into clays by the materials used to produce certain shades of color. Thus for chocolates, browns, black, recovered manganese, and umber are frequently employed. The latter is seldom free from gypsum.

The physical properties of the finished wares are receiving greater attention than formerly, though the requirements of architects should be more rigorous.

It is very important that brick and terra-cottas be burned to such density that they absorb very little water

and suffer no decay through the rigor of our northern climate.

Roofing tile, which on account of the light roof-construction long in vogue in the United States, have but recently been introduced in larger amount, with substantial building, both on account of their technical excellence and decorative character, should be particularly dense and resistant to weathering influences.

The same applies to paving material. Sidewalk blocks and paving-brick are now frequently required to show less than one per cent. absorption of water by weight.

Floor-tile are not subjected to as severe conditions, but if they do take up more than from three to four per cent. by weight of water, they become difficult to keep clean from the grinding of dirt into their pores.

The following data, averaged from a considerable number of tests made on commercial wares of all makers represented in our market, will show that while there is much that amply fills all requirements, the average by no means does.

WATER ABSORPTION OF FLOOR-TILE.

	Percentages by weight.	
Color of the clay.	Extremes.	Average.
Salmon	1.5 to 9.1	5.8
Buff	1.9 to 7.2	4.6
Light gray	1.9 to 8.5	5.8
Dark gray	2.0 to 5.8	4.4
Chocolate	0.0 to 7.4	4.8
Red	1.5 to 8.4	6.0
Black	4.4 to 10.3	7.5
Fawn		8.3

In encaustic tile, it is important that the clay constituting the "backing material" be fully as dense as the

clays making the design inlaid in the face. Where this is not observed the tile are in danger of certain destruction wherever they are exposed to wet and frost, as on the floors of open vestibules and verandas.

The process of destruction is quite the same as that already pointed out in the case of porous glazed brick, subjected to similar exposure. A porous "backing-clay" takes up considerable water, which on freezing does not find room for expansion through a nearly impervious surface. In consequence these nearly vitreous surface-clays, making the design are very soon spalled off, through ice-pressure. This is particularly the case in ware made by the English plastic process. In this the surface bodies, known as "Jaspers" are very dense, while the backing, to make it as little liable to warp as possible, is made very porous by the addition of a large proportion of fired clay in coarse granules ("grog"). Exposed to the conditions indicated, the tile are, in the course of one or two winters, ruined completely.

Prime requirements of paving-ware are, further, hardness and toughness. It should certainly not be possible to scratch anything for such use with even hardened steel. Grinding tests and tumblings for a certain length of time in a "rattler," as is used in the foundries for cleaning castings, have been made, with a view to getting factors representing both of the necessary qualities. The results obtained are valuable, but mainly comparative, and no standards have, as yet, been set up.[1]

[1] Geological Survey of Ohio, vol. vii, part 1, p. 192. Edward Orton, Jr.: Clay-working Industries.

CHAPTER XIV.

REFRACTORY MATERIALS.

HE subject of refractory materials is receiving much serious attention from engineers, and the quality of such products, furnished for the various metallurgical operations, is improving with rapid strides. Recognition that the term refractory is altogether relative has gained ground and leading to a more exact formulation of demands, is becoming the proper basis of improvement.

Refractory bodies being used as apparatus and containers for materials and products subjected to various mechanical and chemical operations at high temperatures must, above all things, be infusible at the temperatures to which these are to be subjected; they must not soften, swell up, or otherwise lose shape on frequent repetition of this condition of temperature or such excess of it as the accidents of operating may make liable. Refractoriness to temperature very much beyond this point is not only useless but is often bought at the expense of other qualities, which from this point on, become quite as essential. Such qualities are the ability to resist abrasion, chemical action of the material, or the fuel and disintegration by repeated heating and cooling.

It is not possible, in the compass of this work, to treat

of the subject of refractory materials other than as the potter himself makes use of them for the building of kilns, the making of saggars for holding ware that must be protected from direct contact with the flame and the wads for luting the same against the entrance of fire gases. The potter, then, has nothing to do with any materials, other than clays, belonging to this category. The problems concerning him, in this connection, are those relating to the resistance to temperature, which is seldom as high as in many metallurgical operations; resistance to disintegration under the movements of repeated heatings and coolings, and under the burden of often very great weights, but of no abrasive action, as in the blast-furnace and lime-kiln; resistance to the action of the flame and the fluxing properties of the ash of the fuel, but of no strong chemical influences requiring decidedly basic or entirely acid refractory bodies. Nevertheless, inattention to the demands of the conditions, although these are not as stringent as in most chemical and metallurgical operations, and are, perhaps, for this very reason more often neglected, becomes the cause of a serious drain on many establishments, in the incessant repair of kilns and the loss of saggars. Practical trials, so-called, are usually quite insufficient to draw from them conclusions as to the behavior of the clay on a working scale. Frequently the potter merely places a lump of the clay, that he intends to apply for refractory purposes, on the bag-wall of the kiln or in the "cut" of the fire, and notices if, after its baking in the place of most intense heat, it remains without trace of

fusion or even sintering. Often he may even make a brick or saggar of the clay and expose it similarly to the most intense heat of his kiln, believing that he is thus making a trial under severe working conditions. This is, of course, far from being the case. Only when a large number of pieces are tested continuously under actual conditions of work, are the accidental irregularities of the making of single pieces lost in an average approximating the truth and only subjection to the many destructive influences of continued use, can answer the question of serviceableness. Such practical trials, if properly carried out, are, contrary to the common belief of those unaccustomed to systematic experiment, expensive and long in giving a conclusive answer.

The question, whether the most serviceable refractory materials are being employed, is an open one in most potteries, which seldom reaches a satisfactory answer or is dismissed from all consideration, and the losses entailed are accepted as inevitable, without attaining the assurance that they are so. A knowledge of the chemical composition of the fire-clays and their pyrometric value by direct determination would dispel all such doubts and enable their selection on the most rational basis that the circumstances will allow. In addition to an exact knowledge of the character of the material, it is important to satisfy one's self that the ware made of it, the bricks, tile, saggars, etc., have been burned at a temperature higher than that to which they are afterwards likely to be subjected, in order to prevent the almost certain danger of cracking and the sinking of

arches in fire-brick structures, when ware shrinks on being subjected in use to temperatures higher than those at which it was originally burned.

To this important matter very little attention has been paid. Engineers have never as yet made a specific demand of the manufacturers of fire-brick and tile, that the ware for different purposes be subjected to temperatures which, according to their use, must not fall below certain definitely prescribed minima.

Furthermore, potters very seldom burn their saggars in a special fire at heats higher than they will meet in future use, but burn the green stock continuously in their regular ware-kilns, placing it on top of the bungs, where it usually gets less heat than in the places where the saggers are later likely to be exposed.

Experience has shown that in order to resist repeated heatings and coolings most successfully, refractory wares must remain as porous or even spongy in character at the temperatures reached, as is consistent with the necessary firmness of body to carry the weights they have to bear. This is particularly the case where from position in a furnace or elsewhere the heating is of necessity rapid and the heated surfaces are liable to be struck by cold air. In order to attain this structure it is customary to mix with the plastic fire-clay, which should in itself be so refractory as to burn quite porous at the heat given, at least an equal weight of the same or a similarly refractory clay which has been burned and ground and so sifted that only particles from the size of split peas to beans are used; the finer material

and dust, which would fill up the pores and interstices, producing too compact a mass, are discarded. This material is known to potters as "grog." About potteries there are always sufficient broken fire-brick and saggars to supply the "grog" needed. In the fire-brick yards it is almost entirely substituted by coarsely ground unburned flint-clays. For the best products it is sometimes burned before use.

Clays markedly siliceous remain porous even in the higher heats reached in pottery burning and can be given an open structure by the addition of pure siliceous sand, where they do not already contain it in sufficient amount to burn of that character in themselves. The majority of refractory clays at command contain more or less finely divided free silica and are not only of ample heat-resisting power, but some of these are of notable quality. Yet the reverse of the popular belief, that the refractoriness is in proportion to the free silica present, is true: a belief unfortunately kept alive by the statements in many economic geologies. The origin of this mistaken belief is, that in the comparatively low heats of pottery kilns the greater the portion of uncombined silica, whether occurring naturally in a clay in which the basic oxids are not excessive, or added artificially, the more porous and seemingly more refractory it is. Seger, however, has shown[1] that the systematic addition of silica to a pure silicate of alumina $Al_2O_3.2SiO_2$, whether artificial or a natural kaolinite, reduces the melting-point until the proportion Al_2O_3.

[1] Thonindustrie-Zeitung, 1893 p. 391.

$17SiO_2$ is reached, which melts with the lowest members of the scales which Seger and Bischof have severally set up as refractory standards. Beyond this point the addition of silica causes a uniform rise in refractoriness until the proportion of alumina is so small that it practically disappears from the mixture: proving the high character of both kaolin and silica separately, as refractory agents and the degree of quality lost in their mixture. It must not be thought that because a clay low in basic oxids in proportion to the contained free silica, remains porous in even the hardest pottery fires, that for the refractory products used by the potter, the more siliceous his fire-clays are, the better; particularly as the more siliceous clays are much cheaper and as the use of a sandy clay or the addition of quartz sand to his fire-clay will give the necessary open structure as well as the more expensive "grog."

Practical experience, where made in conjunction with a knowledge of the composition of the fire-clays, has proven that this is not the case. Mechanical reasons, mainly, unfit very siliceous clays for use as saggars; chemical reasons, in many cases, make them unserviceable for the fire-brick of the kilns. It has already been pointed out that the designating of a material as refractory is properly being done more and more in a relative sense, with a statement as to the conditions under which it is refractory. No chemist or engineer would for a moment think of lining a lime-kiln with dinas-brick.

In nearly all treatises accessible to the manufacturer and the public at large, however, refractoriness is still

treated as if it were an absolute quality, inherent in the material itself and without discussion of the extraneous conditions that may break it down. To value a clay directly and solely by its "oxygen ratio" calculated from the analysis, so commonly taught the public by chemists, interesting themselves in the subject is, to say the least, very misleading. All that this ratio is supposed to teach, the relative fusibilities of clays, is more expeditiously and accurately determined by direct fusion in the Deville forge; for the structure of a clay plays quite as important a part in its fusibility as its chemical composition.

The chemical analysis gives a general but not a very accurate clue to its fusibility; but it gives very positive information of the behavior of the clay toward outside chemical agents to which it may be subjected under the influence of heat. As far as any danger from fusing is concerned, any highly siliceous clay reasonably low in basic oxids, would sufficiently bear a pottery fire in itself. But the loss that the potter fears in his saggars is not from fusing but from cracking. Their walls, compared with brick, are comparatively thin and being filled with ware and piled in "bungs" to the height of fifteen feet and more, often have to bear considerable weight. While a brick, forming part of a solid wall of masonry, presents but one front to the fire, saggars are surrounded with the fire-gases and upon cessation of the fire, with the strong draught of the cooling air. They are therefore subjected to more or less rapid changes of temperature, particularly when

placed opposite the kiln-mouths and spyholes. A saggar made of clay burning dense at the heat of the kiln, will not remain intact under such conditions without cracking, and one of a siliceous clay, even when left quite porous in the fire, soon succumbs also, particularly if a portion of the silica is in the form of grains of quartz. It is probable that the well-known property of the swelling of quartz in the fire produces strains, which under the severe conditions the ware cannot stand.

A clay from Perry county, Ohio, which has found not inconsiderable use for making saggars, fire-brick, wads, and other refractory wares for pottery use, has the composition:

	The entire clay Per cent.	The portion insoluble in H_2SO_4 and Na_2CO_3 Per cent.
Silica	74.93	51.52
Alumina	17.19	0.42
Ferric oxid	0.79	0.09
Lime	0.29	0.04
Magnesia	0.46	0.02
Alkalies[1]	1.61	0.38
Combined water	5.44	0.00
	100.71	52.47

RATIONAL ANALYSIS.

	Per cent.
Clay substance	48.24
Quartz	49.72
Feldspathic detritus	2.75
	100.71

[1] Combining weights respectively 34.9 and 34.5.

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	48.53
Alumina	34.77
Ferric oxid	1.45
Lime	0.51
Magnesia	0.91
Alkalies	2.55
Combined water	11.28
	100.00

Thirty per cent. of the quartz would not pass a sieve with eighty meshes to the inch. This clay, burned at the heat of melting orthoclase, gives a yellowish white body, which is very porous and shrinks but four per cent. Saggars made of it, filled with heavy ware, and set in high bungs have an average life of but three and one-half burnings, at the melting temperature of feldspar (orthoclase).

The same clay, made into brick, stood sufficiently well in many instances as the lining of pottery kilns, but whenever brought in contact with basic oxids the destruction was rapid and complete. Used in the mouths, bottom-flues, and arches of a muffle-kiln for slip-glazed stoneware, fired with coal yielding a ferruginous ash, these parts broke down in a few firings. The fire-arches of two boilers built of them, under which the slack of a similar coal, high in iron pyrites, was used, lasted but a few weeks. As the lining of a salt-glaze kiln they melted away very fast.

The reason of the clays succumbing to the action of basic oxids is readily explained from the composition of stoneware glazes themselves.

It was seen that the most fusible silicates containing no reducible metals as lead or zinc, were those approximating the formula $1RO.0.5R_2O_3.4SiO_2$ and that more aluminous compounds formed puckered viscid crusts, but not fusible glasses. In this clay the relation of alumina to silica is as 1.0 to 8.34 and under the action of ferrous oxid and of soda, it would give fusible glasses of about the composition $1FeO.0.5Al_2O_3.4.17SiO_2$, and $1Na_2O.0.5Al_2O_3.4.17\ SiO_2$, which on running off the face of the brick would constantly expose more of it to their destructive action. An aluminous clay would absorb some of the base, forming in time a superficial vitreous coat, but not a fusible glass: it would remain in place as an effective protection to the material beneath.

The wads and plugs used to support the bungs of salt-glazed stoneware and keep them separate during burning, should not be made of siliceous clays resembling the one above discussed, for the reason that the more readily such a clay combines with the alkali fumes the more will it stick to the ware, from the formation of glass at the outer line of contact with it. These plugs cannot, in this case, be struck off without more or less damage to the pieces to which they were attached. Plugs of aluminous clay remain dry and give no cause for sticking.

Stoneware potters using clays that salt-glaze readily are often troubled with the rims of the pieces, that are set on each other, adhering, causing some breakage when the ware is taken apart. Such as have tried it,

will have found that the washing of the surfaces of contact with flint, as is done with saggars in the white-ware potteries, may often aggravate the trouble. The reason for this is patent from the experiences and arguments given, as is also the remedy sought. China-clay or a fire-clay, as near the composition of kaolinite as possible, would give a proper wash for the purpose. On the other hand, wads used for luting the saggars holding ware that is not burned in the open fire, which serve mainly as a yielding bed for each saggar as it is placed on top of that last set and enables the kilnman to run his "bungs" up straight, should be as siliceous as possible. Made of such clays they will, by their lower shrinkage and binding action, from their remaining more open in a fire free from basic fumes, adhere to and break the saggars less than other clays. For such purpose the clay cited proved excellent.

The example of this material sufficiently illustrates the value of the chemical analysis in estimating the suitableness or unsuitableness of a clay as a refractory material under different conditions, entirely aside from its ability to bear mere temperature without fusing. Use of refractory materials is still made with most unnecessary waste, both in the employment of clays that are too good and of those which are altogether inadequate for their application. The responsibility for this must rest largely with the very one-sided study that chemists have, as a rule, made of fire-clays, in looking solely to their relative fusibilities and failure to instruct the public in the physical and chemical conditions that

a refractory material has to resist in different places of its application, which often are of such importance that the relative fusibilities are, beyond a certain point, of very minor significance.

The best plastic clays for saggar-making have thus far proven to be the tertiary clays of New Jersey,[1] particularly those that with not too high a percentage of uncombined silica contain considerable organic matter that burns out in the fire giving the clay a very porous structure. Clays of low-binding power when dry, however, as New Jersey clays are apt to be, must be worked very carefully that the green ware does not crack before it comes into the fire.

The flint-clays of south-eastern Ohio form, when burned, an excellent material as "grog." Some of these are very pure, having almost the composition of kaolinite, as the following :

	Per cent.
Silica	46.54
Alumina	38.47
Ferric oxid	0.77
Lime	0.29
Magnesia	0.23
Alkalies[2]	1.38
Combined water	12.98
	100.66

The clay, in spite of its composition was, when very finely pulverized, extremely difficult to decompose with

[1] For a valuable description of New Jersey clays see "Report on the clay deposits of Woodbridge, South Amboy, and other places in New Jersey." 1878, by George H. Cook, State Geologist.

[2] Combining weight, 40.8.

sulfuric acid. Even after a treatment of fifty hours with the acid, it left, after washing with sodium carbonate, a residue of 7.54 per cent.

From the fact that in many instances these flint-clays are more refractory than the available plastic clays used as the bonds in the fire-clay products, and that in consequence fire-brick are commonly graded into first and second qualities, as they contain a greater or less amount of flint-clay, the idea has become rather common that all flint-clays are highly refractory. This is far from being the case; not a few of low quality, have from this mistaken idea, come extensively into use.

An example of one so used is a flint-clay of Beaver county, Pennsylvania, of which the following is the analysis:

	The entire clay contains	The portion insoluble in H_2SO_4 and Na_2CO_3
	Per cent.	Per cent.
Silica	65.85	36.86
Alumina	22.87	2.19
Ferric oxid	1.14	0.11
Lime	0.53	0.42
Magnesia	0.37	0.07
Alkalies[1]	2.01	0.47
Combined water	6.93	....
	99.70	40.12

RATIONAL ANALYSIS.

	Per cent.
Clay substance	59.58
Quartz	30.42
Feldspathic detritus	9.70
	99.70

[1] Combining weights respectively 45.5 and 39.7.

PERCENTAGE COMPOSITION OF THE CLAY SUBSTANCE.

	Per cent.
Silica	48.66
Alumina	34.71
Ferric oxid	1.73
Lime	0.18
Magnesia	0.50
Alkalies	2.59
Combined water	11.63
	100.00

In a kiln burned to the melting of feldspar the clay becomes very dense and it melts in the Deville furnace together with Seger's pyrometric cone twenty-six, so that it would be looked upon as a fire-clay of the lowest grade.

According to the oxygen ratio (Feuerfestigkeitsquotient) of Bischof $\frac{\frac{O \text{ in } Al_2O_3}{O \text{ in } RO}}{\frac{O \text{ in } SiO_2}{O \text{ in } Al_2O_3}}$ which is 1.24 in this clay, it is not even worthy of being designated a fire-clay, as the lowest member of the scale he admits to this classification is the clay of Niederpleis on the Sieg, with the ratio 1.64.

In the examination of a fire-clay, first a chemical analysis is required to determine how it will resist chemical and mechanical influences incident to its use. From this the oxygen ratio (Feuerfestigkeitsquotient) may be calculated, according to Bischof,[2] to give a gen-

[1] Using, however, the old formulas and equivalent weights and calculating iron as ferrous oxid with the RO elements.

[2] C. Bischof, Die feuerfesten Thone, Leipzig, 1876; Transactions of the American Institute of Mining Engineers, Virginia Beach meeting, February, 1894; H. O. Hofman and C. D. Demond: Some Experiments for Determining the Refractoriness of Fire-clays.

eral idea of its relative fusibility. The only value of this is to be able to institute a comparison of the clay with others of which the analyses are available, but of which no direct determinations of fusibility are recorded. Bischof's quotient is preferable because it is best known and because no other can, after all, bring in the main factor of variation, which depends on the physical structure of the clay.

Next, the direct determination of the relative fusibility of the clay is made. It is most satisfactory if the standing of the clay is referred to Seger's pyrometric scale. This direct determination is made according to Seger and Cramer[1] by forming small tetrahedra of the clay to be examined, two centimeters high by one centimeter on the edges of the triangular base and inclosing these, together with similarly formed pyrometers of the higher members of Seger's pyrometric scale, in a small covered crucible, five centimeters high by four and one-half in diameter, the walls and cover being five millimeters thick. The material of which these crucibles are made is a mixture of equal parts of alumina and china-clay, burned to a "grog," in as high a heat as is at command; for forming, the material is rendered plastic by the addition of the necessary amount of unburned china-clay. In the bottom of the crucible a layer of the alumina-china-clay grog, powdered fine, is packed and the bases of the trials pressed into it, to prevent their being upset. The crucible with its trial pieces is set in

[1] Thonindustrie-Zeitung, 1893, p. 1281. Also, Transactions of the American Institute of Mining Engineers, Florida Meeting, 1895. H. O. Hofman: Further Experiments for Determining the Fusibility of Fire-clays.

the Sefström or Deville furnace upon a block of refractory material of sufficient height to raise it into the focus of the heat generated by gas-retort graphite in pieces the size of a hickory-nut and maintained by a gentle blast from a rotary blower.

The member of the pyrometric scale melting coincidently with the clay being tested gives the numerical index of its refractoriness. As the trial pieces are not under observation during the heating several tests at greater and less heats are necessary to fix the right degree.

The composition of these higher pyrometers of Seger is as follows :[1]

Cone number.	Chemical composition.
21.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 4.4Al_2O_3.\ 44SiO_2.$
22.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 4.9Al_2O_3.\ 49SiO_2.$
23.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 5.4Al_2O_3.\ 54SiO_2.$
24.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 6.0Al_2O_3.\ 60SiO_2.$
25.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 6.6Al_2O_3.\ 66SiO_2.$
26.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 7.2Al_2O_3.\ 72SiO_2.$
27.	$\left\{\begin{matrix}0.3K_2O\\0.7CaO\end{matrix}\right\} 20Al_2O_3.\ 200SiO_2.$

[1] Thonindustrie-Zeitung, 1893, p. 1252.

Cone number.	Chemical composition.
28.	Al_2O_3. $10SiO_2$.
29.	Al_2O_3. $8SiO_2$.
30.	Al_2O_3. $6SiO_2$.
31.	Al_2O_3. $5SiO_2$.
32.	Al_2O_3. $4SiO_2$.
33.	Al_2O_3. $3SiO_2$.
34.	Al_2O_3. $2.5SiO_2$.
35.	Al_2O_3. $2SiO_2$.[1]
36.	Al_2O_3. $2SiO_2$.[2]

To receive the designation "fire-clay," a clay should not melt more easily than pyrometer twenty-six.

High grade fire-clays seem often of low binding power. While sufficient in this property, for the making of brick and of the ordinary saggars a considerable amount of bonding clay is yearly imported from Germany for the making of glasspots and other large ware. It would certainly seem that our great wealth in clays must include deposits having the necessary physical qualities coupled with high refractoriness and it is important that systematic examinations be made in this direction also the data being furnished with the analysis and relative fusibilities.

Finally, in accordance with the character of the clay and the use of the products which are to be made of it, the chemist should recommend the minimum temperature of their burning.

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[1] Zettlitz kaolin, with which also the preceding ones are made.

[2] Shale of Rakonitz.

CHAPTER XV.

BURNING THE WARE.

THE important chemical operation to which all pottery wares are subjected, is that of burning or firing. This operation is carried on in kilns, that vary widely in character and construction, a variety, for which the different kinds of ware and the questions of handling and setting in the kilns, to best advantage, present many good reasons. But it cannot be denied, that in many instances, the mechanical considerations which have determined the style of kiln, have been accepted without a clear understanding or due appreciation of the operation of burning in itself and its effects on the ware.

These are among the most important of the subject. The construction and size of the kiln, the character of its fire-places, and the means of creating and regulating the draught, must all be such, that for the purpose for which the kiln is built, it is possible:

1. To obtain the necessary temperatures required in the proper intervals of time and to hold them at pleasure, as the work may demand.

2. To get as uniform a temperature throughout the kiln as possible by the ability to direct or advance the heat in its different parts, as the progress of the fire may require.

3. To be able to get the chemical quality of flame needed for any operation at will.

4. To get the maximum heat effect with a minimum of fuel.

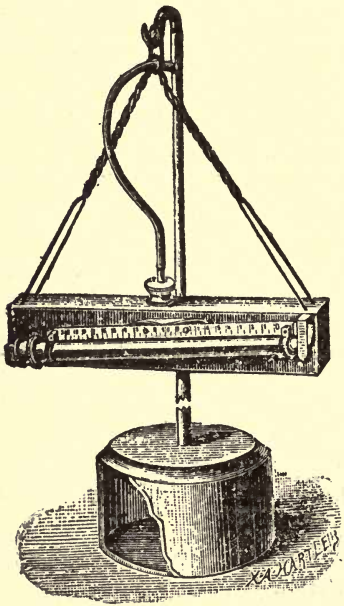
From the standpoint of the chemist, who accepts the methods and apparatus of empirical work, but must modify or add to them, so as to eliminate the elements of chance, the first consideration in firing, bears on the question of production and regulation of the draught. As the ultimately high temperatures produced in all pottery kilns causes a sufficiently rapid movement of the gases to bring an abundance of air into the firings for the combustion, many forms of kilns have no regular chimney. The smoke and products of combustion either escape from the imperfectly closed top, as in the old brick-clamp or from openings in the arched crown, as in the English pottery kiln. The latter, it is true, is as a rule, topped with a cone, intended to collect the gases from the various openings and convey them above the roofs of the surrounding buildings. It acts, in a measure as a chimney but having a large radiating surface it acts very poorly, when a positive draught in the kiln is most needed, namely, when the temperature in the kiln is still low. Besides, its form precludes the possibility of regulation with it except to a very limited extent. As the admission of air into the kiln is determined by the speed with which the products of combustion are withdrawn and by the greater or less obstruction presented to the air at its entrance; in kilns of the above type this regulation is mainly effected in the latter way.

Such a method of regulating the volume of air needed, by more or less obstruction at its entrance, is very troublesome and uncertain. There must of necessity be many places of entrance to attend to affecting the draught more or less by their size, shape, and the position of the fuel in the firings. The regulation of these, individually, must at most be the veriest guesswork. By the withdrawal of all the products of combustion through a single stack, of such dimensions to produce at all times a draught in excess of the needs, and controlling this with a single damper, positive in its action, the pressure in the kiln can at will be brought to any definite degree below that of the atmosphere and produce a proportionate influx of air through all openings. The individual air inlets can then be adjusted separately, if need be, to the requirements of each fire-place, or manipulated to throw the flame to the top or crowd it to the center and bottom of the kiln, as the progress of the heat in different parts of the kiln may require.

The draught in the chimney determines the proportion of air entering the kiln, and therefore the character of the combustion and the quality of the flame.

Hence, it is necessary to determine, by analysis, the composition of the gases leaving the kiln through the stack and at the same time to note, by a continuously acting kiln-barometer, the pressure in the kiln below that of the air, at which the gases are of the composition found. A few of such analyses, during the progress of a firing, at times when the kiln-mouths have just been charged with fresh fuel and when the same has well

burned down, will establish the proper kiln-pressures for admitting the needed amount of air at the different stages of fire, so that the damper can be handled altogether by the reading of the kiln-barometer and gas-analyses will only be needed as occasional checks.



KILN-BAROMETER OR DRAUGHT-METER.

For the gas analyses, the Orsat apparatus is convenient, though even a simple Bunte or a Cramer carbonic-acid pipette is sufficient to gain the necessary knowledge of the quality of the gases leaving the kiln. The most convenient kiln-barometer or draught meter is a modfied form of that of Scheurer-Kestner.[1] It consists of a tin box having a glass guage tube at the side, opening into the box at its lower end and into the air at the upper, inclined at an angle of nine degrees, through which the rise and fall of the liquid in the box is amplified ten-fold, making the readings of the slight changes of level possible with the unaided eye. The guage is supplied with a

[1] Thonindustrie-Zeitung, 1891, p. 696; Dr. Julius Post: Chemisch-Technische analyse, vol. II, p. 73; Braunschweig, 1890–1.

scale and suitable metallic fittings attaching it to the box and protecting it against breakage. The box is filled with carbon oil to the zero mark on the guage-glass, when it hangs level. The opening through which the box is filled is closed with a thumb-screw pierced with a piece of brass tubing. By means of a piece of rubber hose attached to this and a porcelain tube walled air-tight into the kiln or chimney, the atmosphere of the latter is connected with that above the oil, communicating the kiln-pressure to it. Instead of a porcelain tube a duct may be walled from the kiln to the top of the "hob" surrounding the same and the bell-shaped iron foot of the stand of the instrument placed over it. The rubber hose connection of the kiln-barometer is then attached to the gas-pipe upright, as shown in the cut, and the communication with the kiln established through the duct, bell, upright pipe, and hose to to the box. Through the porcelain tube used to communicate the kiln-pressure, where this is used, the samples of gas for analyses may be taken, though it is also well to take such samples from the top and bottom of the kiln, by other porcelain tubes, properly let into the walls of the same at the respective places.

Unfortunately, these simple devices for attaining a positive knowledge of the character of the fire and helping it in the condition desired by regulating the damper with reference to distinct stack-pressures, have not, as yet, found entrance into our potteries. Firing is looked upon as a mysterious operation and even experienced burners do not attack it, in new kilns, or with new

wares, with the confidence that the possession of positive data and a knowledge of their meaning would give them.

The majority of even the best kilnmen waste considerable fuel by the admission of excessive amounts of air to the kiln. How great this waste is, few potters perhaps realize. A glost kiln fired with crude petroleum sprayed into the kiln-mouths with compressed air from atomizing burners required 1,050 gallons or 3,135 kilograms of the fuel. The kilo of oil required about 14.35 kilos of air for its combustion and probably had a calorific value of 10,000 heat units.

Analyses of the flue gases proved that throughout the burning about 175 per cent. of air was used, as the kiln was ordinarily fired. Subsequent firings showed that although lead glazes were being burned an average consumption of 110 per cent. of air was not only ample for smokeless combustion, but did not endanger a loss of ware by reduction of the lead of the glaze. Hence, sixty-five per cent. of the theoretically necessary amount of air was admitted to the kiln, above its practical needs, amounting to 29,239 kilograms. At the finish of the burning the gases left the kiln with a temperature sufficient to melt an alloy of twenty per cent. silver, eighty per cent. gold, or about at the temperature 1,045° C. The average heat of the gases leaving the kiln from beginning to end of the fire was therefore 523° C. Taking 0.2377 as the specific heat of air, each kilogram of the excess of the same took away needlessly 124.32 heat units or 3,634,660 in all: a quantity which required the combustion of 122 gallons of the petroleum to sup-

ply. At subsequent firings, a careful regulation of the draught, according to the practical needs, effected a saving of about three barrels of oil to each burning.

The above example is by no means an extreme case ; on the contrary it is probable that in coal-firing an excess of upwards of 100 per cent. of air is the practice. In an ordinary boiler-firing it is customary to allow an excess of thirty per cent. of air, in order to insure ample contact of the solid fuel with the same, on the grate-bars. In firing a pottery kiln, the excess of air may be less, because of the better opportunity for combination in the greater distance of travel under far higher temperatures than in the boiler, though how much less, is a matter of experience, depending upon the fuel, the kiln temperature, the character of the firings, and the distance the gases have to travel in the kiln, before reaching the exit.

In order to distribute the heat as uniformly as possible throughout the kiln, it is important that the combustion take place mainly beyond the fire-places and that these act rather as generators. Those parts of the kiln exposed to radiation from the fire-places, known as the "cuts," are invariably hotter than the others and this condition is greatly aggravated, when the fuel lies shallow and is mainly consumed on the grate-bars. The heating of the kiln does not, in this case, it is true, take place entirely by radiation and conduction, for through the dissociation of the products of combustion in passing this heated zone, combustible gases are formed which recombine at the lower tempera-

tures in the interior of the kiln. But the absorption of heat in the "cuts" by the dissociating gases is never sufficient to reduce the heat to a moderate difference from that in the rest of the kiln. For this reason, the fire-places, instead of being broad and shallow, should be narrow and deep, approaching the character of fuel-gas generators. The gases leaving them being mainly reducing in character, burn in their progress through the kiln, as by diffusion or by striking solid objects obstructing their way, they become thoroughly mixed with the air entering through doors, air-openings, and spy-holes. It is only where the firings are of this character that it becomes possible to burn with a relatively small excess of air and effect the economies incident to so doing. For where the fuel lies shallow on the grate-bars air channels soon work through it, admitting excessive amounts of air ascending in compact columns, which afterwards comes but little into play in combustion, where the firings send the complete products of combustion and not combustible gases along with this air into the kiln. As there is in this case absolutely no way of knowing the proportion of grate surface sending nearly pure air into the kiln, and as there is no way of regulating it, a reduction of the general draught of the kiln until the flue-gases have the proper composition, would often be attended by a cutting down of the combustion until insufficient for producing the necessary rise in temperature. Only where the kiln-mouths send reducing gases into the kiln and the needed excess of air enters through openings that can be

manipulated and controlled is the fire absolutely in hand as then, by closing the air inlets more or less, the draught of the stack can be made to act more or less on the fire, sucking the fuel-gases in the proportion wanted.

It is a familiar fact to all who have had to make analyses of furnace-gases, that columns of gases, even where great chemical affinity exists between them and the temperature is favorable to combination, may travel side by side with little diffusion and combination. It is necessary, therefore, to make the distance of travel in the furnace of sufficient length and provide that the gases strike solid objects and are compelled to turn on themselves to effect mechanically as thorough a mixture as possible. The most rational kilns, then, are those working on what is known as the "down draught" principle. In these the gases rise from the fire-places to the crown against which they strike and are compelled to descend between the bungs of saggars or of ware to the flues under the floor which lead to a center tunnel connected with the stack. The striking against the crown of the kiln, the horizontal movement under the same, with the mixture effected by the impeding tops of the bungs of ware and the downward movement, most effectually breaks up any tendency of the gases to move in separate channels.

The building up of the ware in the kilns and the arrangement of the flues and the tunnels to the stack must be made with careful consideration to the end that the gases from the different fire-places meet similar frictional resistances throughout their long distance of travel;

otherwise the combustion in different parts of the kiln will vary so as to make it impossible to burn it with any approximation to uniformity. And, furthermore, it must not be forgotten, that as the gases have to travel at least three times the distance they do in an up-draught kiln, and where the stack is outside of the kiln, at least four times this distance, the frictional resistance they encounter is proportionately as much greater and must be overcome by a proportionately greater draught or a corresponding reduction in the speed of combustion and cooling will have to be expected. This fact has often been overlooked where an up-draught kiln has been changed into a down-draught, by closing the crown holes and carrying a center stack in the kiln to just above the crown, the cone carrying off the smoke and creating the draught as before, expecting an increase of this draught without any alteration. Where in such a case it was attempted to burn glazes high in basic oxids, particularly sensitive ones and such of a composition causing devitrification if they are not rapidly cooled, disappointment at the down-draught principle has unjustly ensued. With a suitable provision for the necessarily greater draught required to draw the fire-gases through their longer and more tortuous course, all the seeming advantages of the up-draught kiln can be obtained, without sacrifice of the more thorough combustion aimed at in the other construction.

The dissociation of the products of combustion in the "cuts" of the kiln as well as the production of combus-

tible gases in the producer-like fire-places yields sufficient length of flame for the longer distance of travel, in the down-draught kiln, even with short-flamed fuel. This cannot, however, be counted on to extend the effect of the fire with practical uniformity of temperature to an indefinite distance in the kiln. As the flame, after some distance of travel toward the outlet, becomes freighted with the products of combustion, these, together with the inert gases that it necessarily carries with it, nitrogen and the water vapor derived from the moisture in the fuel and the oxygen which it contained, may grow to such proportions as to extinguish it, even though it still contains combustible products and an excess of oxygen. There is then a practical limitation to the distance of travel of the fire-gases, consistent with their being still effective, which fixes the dimensions of kilns. When these exceed a capacity of 3,500 cubic feet it is difficult to regulate them so as to burn sensitive products uniformly.

The regulation of the English pottery kilns, which are the common type in use in most of our ceramic industries, must be effected altogether by the manipulation of the air inlets. In up-draught kilns, the draught being as a rule much too strong, the bottoms are most liable to be hard, while in down-draught kilns the reverse is the case and it is often difficult to bring the lower ware to the required temperature. In the latter case the flame must be crowded to the center and bottom of the kiln, which is done in admitting air over the kiln-mouths by withdrawal of the regulating brick. The air sucked in

through the exposed opening rises in a column next to the kiln-wall to the crown and forces the fire-gases inward. Where this source of air is insufficient the fire-doors will often have to be given more or less opening. Amounts of air, largely in excess of the needs of combustion, are in this manner often necessarily introduced into the kiln for regulation, and as previously pointed out, involve a correspondingly greater consumption of fuel. Where the bottoms of the kiln get too hard it is, of course, necessary to cut off as near as possible all air supplies over the fire, which tend to crowd it down. Serious defects interfering with the regulation must be met by permanent alterations in the kiln, as increasing or reducing the size of the crown holes, the flues, and of the cone, or of admitting air into the latter over the crown. But the variations in draught due to the wind, and the changing pressure of the atmosphere, and the rise in temperature of the kiln, which in a kiln with a stack and damper can be met by the setting of the latter, can in these be counteracted by the manipulation of the air inlets alone.

The rapidity of firing a kiln is determined by the draught, the size and number of the fire-places, the intervals of time in which fuel is supplied to the fires and the weight and character of the ware contained in the kiln.

Thin-walled ware, that is reasonably uniform in section, as most dishware, can be burned and cooled quite rapidly without danger of loss in the kiln or creation of a brittle product as one with internal strains tending to shatter it. It is well to have kilns for the manufacture of

this, with a very strong draught, providing the kiln-mouths be correspondingly large or numerous to take the fuel for a plentiful combustion. It is then possible to push the productivity of a kiln, if the manufacture demands it.

Glazes having a tendency to cloud or devitrify must be fired and especially cooled rapidly. With these it is not infrequently the custom to "draw the fires," as it is called. As soon as the required temperature has been reached the grate-bars are let down, the fire raked out of the mouths and extinguished.

Sanitary ware, terra-cottas, tile, and all varieties of brick should be fired and cooled slowly. In all of these the bodies are thick and opportunity must be given the hygroscopic and especially the combined water of the clay to leave it slowly so as not to incur the danger of warping, shattering, or cracking the pieces. It is likewise important that such products be cooled slowly, whereby they undergo a sort of annealing process that is very essential to their life. Building terra-cottas and the vessels used in sanitary plumbing often have thin walls attached to thick ones; the unequal cooling of which is unavoidably associated with the rapid cooling of non-conducting products, brings about unequal and severe strains, making these pieces sensitive to sudden changes of temperature and light blows or jars. All paving material is sensibly toughened by slow cooling. The kilns for these products need not, therefore, have so great a proportionate fire-place volume to the volume of kiln space and the draught may be correspondingly

less. The slowing of the fire by charging the furnaces with baitings of fuel at greater intervals is only possible with a corresponding reduction of the draught. Where the fire is maintained with solid fuel the temperature should rise in regular throbs or pulsations corresponding with the baitings. These should burn down to clear glowing coals, before the mouths are again charged, but not so far that the temperature begins to recede from the point reached. The progress of the heat must be continuously upward and as uniform in the periods of its rising as possible. Where then this progress is too great the fuel must be made to burn more slowly by cutting down its draught.

The stormy evolution of gaseous products, when fresh baitings of fuel are put on the fires, produces periodically a reducing atmosphere of greater or less duration in the kiln; if this is succeeded each time by a clear oxidizing atmosphere, no danger of the reduction of even lead glazes need be feared. In fact, the alternating of a short period of reducing influences followed by a longer one of oxidation is in many cases preferable to a continuously oxidizing fire throughout the burning. All fossil fuels, oil, coal, and the fuel-gas made from it, as well as natural gas, contain considerable sulfur, which, on burning, is absorbed in an oxidizing atmosphere as sulfuric anhydride by glazed surfaces, causing unsightly separations of crystalline sulfates in the melted glass.

Through the action of reducing gases, these sulfates formed on the surfaces of the glaze are decomposed, the

sulfur being carried away with the other gases of combustion as dioxid.

Seger[1] found that the clay of Birkenwerder, rich in lime and iron, glowed for two hours in an atmosphere of sulfur dioxid, and air took up 13.6 per cent. of sulfuric anhydrid. By heating it again in a reducing atmosphere this could be entirely expelled. Through this discovery he found an explanation of the phenomenon that clays of this type, which in the ordinary intermittent kilns fired with coal produce a yellow or cream-colored body from the formation of a lime-iron silicate, in continuous or gas-fired kilns, generally burned red or were flashed with red. In the latter the kiln-atmosphere is generally continuously oxidizing. Under this condition the lime in the clay absorbing sulfuric acid from the fire-gases does not combine with the iron and leaves the latter to impart its red color to the product. It has been found that in following Seger's suggestion of manipulating the draught in these kilns so that at regular intervals the kiln-atmosphere is strongly reducing, these clays can be burned uniformly to a cream color as well as in the intermittent kilns fired with solid fuel.

In the case of tin-enamels, the writer has observed that when burning in kilns fired with crude petroleum sprayed into the mouths with compressed air, so that the fire is continuously oxidizing, they are very liable to have a pink cast, while burned with an alternately reducing and oxidizing flame they become snowy white. These instances will suffice to show that the smoke

[1] Thonindustrie-Zeitung, 1877, p. 22.

issuing at regular intervals from the ordinary kiln is not only harmless, but may play a very useful roll, provided that the burning be so conducted that too much fuel is not wasted and the kiln-temperature is not depressed in throwing too much coal on the fires at each baiting.

The useful results of temporary and recurring reducing periods in the burning, unwittingly attained in firing with solid fuels can, of course, be just as easily obtained with oil and fuel-gas. But as these are often used, mainly, from a supposed advantage of the ease with which they are handled to give a smokeless combustion, and as to the average mind this is the perfection of firing regardless of the results sought, it is difficult to make the potter understand that this may be associated with practical objections.

The phenomenon that potters commonly ascribe to the effect of sulfur in the coal is due to excessive reduction in glost-kilns, through careless firing. It is a reduction of the lead of the glaze so that the latter turns black and it comes when the fireman has been careless about clinkering his fires and has not kept the grate-bars clean. The phenomenon may in so far hang together with sulfur in the coal, that inasmuch as the sulfur is mainly present as iron pyrites, when this is high, the large amount of iron slag or clinker that is formed requires especial watchfulness, to prevent its shutting off the air supply coming through the live coals.

Our pottery kilns, like all the older apparatus using high temperatures that discharge their products of combustion directly into the air, without being compelled

to first give off their surplus heat, where it can again be utilized for the burning, are under the most favorable conditions of operation very wasteful of fuel.

The most successful application of the regenerative principle, in which a greater effect is obtained from fuel, than perhaps, in any other apparatus, is the ring-brick kiln of Hoffmann and Licht. Few of these have as yet been built in the United States and few of the regenerative gas-kilns of Mendheim and of Dunnachie. Ignorance of the progress made in ceramic industries elsewhere, are in part responsible for this, though valid commercial reasons connected with the cheapness of our fuel and the generally higher price of labor, have made people slow to lock up the greater amounts of capital involved in these modern kilns. There is no reason, however, since the progress made in this direction by the iron and glass industries, why the pottery industries should not follow; especially as in these the application is much more simple.

Special "stoves" and "regenerators" for taking up the waste heat and imparting it to the air for the combustion being unnecessary, as a battery of kilns suitably connected, with their contained ware, act in turn in this capacity; the kilns in advance of the one in fire taking up the waste heat from the products of combustion before these are turned into the stack, while the air for the combustion serves to cool those which have been fired and comes hot to the one burning.[1]

[1] Groves and Thorpe: Chemical Technology, Vol. I., Fuel and its Applications; Thonindustrie-Zeitung, 1877–1895.

INDEX.

ACETATES in white lead deleterious for preparation of glazes therefrom 125
Alloys of Prinsep 30
Analysis of clay. Necessity for accuracy in, 3; separation of silica and alumina, 4; alumina and ferric determination, 5; impurities in reagents, 5; impurities in distilled water, 6; determination of potash and soda, 6; proximate analysis, 6; "clay substance," 8; "rational analysis," 8; calculation of. to dried substance, 13; for white enameled brick, 140, 144; for saggars, fire brick, etc 165, 170
BANKO ware 78
"Barbotine" ware 73
Bischof's opinion of rational analysis 9
Biscuit, analysis of, 13; calculation of mass for 13
"Blue calx," composition of 120
Boron in glazes, 14; action of boron in glazes, 50; volatilization of 125
Brick, white enameled 139
Broginarts' classification of ceramics 41
Burning, 175; draught in the kiln, 176; analysis of kiln gases. 177; draught meter, 178; firing, 179; uniform distribution of heat, placing of the ware in kilns, down and up draught kilns, 183; rapidity of firing, 186; reducing action of fresh fuel, 188; regenerative kilns 191
"C. C." ware 43, 117
Ceramics, classification of 41
"Checking" 21
Chemical ware 78
China-clay 96

Chromic oxid use as coloring material..... 133
Clay analyses. Kaolin from Nelson Co., Va., 10; kaolin from Zettlitz, 37; from Western N. Carolina, 37; weathered shale, 60; red-colored clay, 61; of clay for yellow ware, 66; flint clay, 68; for stoneware, 80; Albany slip clay, 83; slip clay, 86; kaolin, 95, 96; from Lawrence Co., Ind., 98; from Inyo Co., Cal., 98; plastic kaolin from Florida, 100; New Jersey clay, 101; from Jefferson Co., Mo., and Calloway Co., Ky, 102; Cornwall stone, 110, 112, 114; from Texas..... 115
Clay, importance of careful sampling for analysis of, 1; necessity for careful analysis of, 3; purification of, by washing and sifting, 3; action of sulfuric acid upon.. 9
Clay, physical properties of, 15; coloring of burned, 15; physical testing of, 16; mechanical analysis of, 17; plasticity of, 18; binding power of, 20; burning test for, 21; for floor tile and paving brick, testing for porosity, 24; shrinkage..... 24
Cobalt oxid, composition of commercial..... 132
Copper oxid, use as coloring material..... 133
Cornish stone..... 118, 119, 120
"Crazing," 48; cause of..... 50
Cream colored ware, 117, glazes for..... 122
DISTILLED water, impurities in..... 6
Doulton ware..... 78
"Dunting"..... 21
Dust pressed articles..... 25
ENAMEL, description of the term, 46; see also glazes
Enameled brick, 139; separation of glaze from, by freezing and thawing..... 147
Enameled tile, 127; glazes for..... 129
Engobe ware, 65; for white enameled brick..... 142, 145
FAIENCE..... 45, 62, 66

Fayal pottery 43
Feldspar, analysis of Rörstrand, 37; analysis of, from N. Y., 37; analyses of commercial, 108, 109; Cornwall stone, 110, 112, 114; from Texas 114
Ferric oxid, use as a coloring material, 136; analysis of "Crocus Martis," 136
Fire brick 158
Flint, [see quartz]
Flint clays, analysis of 170
Flint glass, analysis of 52
Frit melting 125

GLAZES. Preparations of samples for analysis, 13; containing boric acid, 14; necessary qualities of, 48; crazing and shivering, 50; action of boric acid, 50; silica, 51; alumina, 51; formula for, 51; distinction between "raw" and "fritted," 53; example of calculation of, 54; action of sulfates in, 55; for red ware, 58; for Rockwood pottery, 62; for yellow ware, 71; for Rockingham ware, 72; salt glaze, 81; slip glaze for stoneware, 83, 91; for white granite and C. C. ware, 122; for majolica and enameled tile, 129; for white enameled brick, 141, 145, 146; action of frost upon glaze for enameled brick 147
Granite ware 117

HEINTZ'S glass mixtures 32
"Hotel china" 44

KILNS, for testing clay, 23; dimensions of, 28; down draught, 183; [see also burning]

"LIMOGES" ware 73

MAJOLICA, 127; glazes for 129
Majolica and faience, distinction between 45
Manganese, use as a coloring material 134
Marble, analysis of Carrara 37

Mica, in clay, 3; clay containing products of the decomposition of 11
NICKEL oxid, use and composition 133
PENNSYLVANIA Dutch pottery 62, 65
"Plastic kaolins" 100
Porosity of floor tile and paving brick, test for 24
Prinsep, alloys of 30
Pyrometry 26
QUARTZ, in clay, 9; analysis of Norwegian, 37; analysis of Illinois, 38; from N. J. and Ill. analysis, 105; from Tenn., 106; from Ky. 107
"RED ware," 43, 58; glaze for, 58; articles made of, 61; examination of materials for 64
Refractory materials 158
"Rockingham" ware, 66; glaze for, 72; articles made of, 73; examinations of materials for 73
Rookwood pottery 62
SAGGARS, clay for 163, 165
Sampling of clay, directions for 2
Sand, [see quartz] .....
Seger & Aron's rational analysis of clay 8
Seger's cones, 33; mixtures for preparing, 38; use of, 40; composition and use of 173
"Shivering," 48; cause of 50
Shrinkage in firing, test of 24
Silica, distinction between quartz and combined, 9; separation from alumina and ferric oxid 4, 5
"Slips" 65
Stoneware, 77; articles made of, 77; use of, in chemical industries, 78; clay for, 79; glazes, 81; examination of material 92
Sulfates objectionable in glazes, 55; in floor tile and terra cotta, 153; action in the kiln 189
TEMPERATURE of the kiln, methods for determining ... 26

Terra-cotta, 149; shrinkage in burning 152
Thenard's blue, composition of 120
Tile, enameled, 127; glazes for, 129; floor, 149; roofing, 156; encaustic 156
Tin oxid, use in enamels 137
UMBER, use as a coloring material 134
Uranium, use as a coloring material 135
VICAT'S needle 18
WATER, impurities in distilled 6
"W. G." ware 43
White granite ware, 117; glazes for 122
White lead, deleterious influence on glazes of acetate contained in 125
White ware 93
Whiting, analysis of 38; composition of 116
YELLOW ware, 66; preparation of the clay, 67; glaze for, 71; articles made of, 73; examination of materials for 73

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